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POLYCHLORINATED DIBENZO-P-DIOXINS

AND

POLYCHLORINATED DIBENZOFURANS

AND

OTHER ORGANOCHLORINE CONTAMINANTS

IN FOOD

AUGUST 1988

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MOE

Ontario
Ministry of Agriculture and Food
Jack Riddell, Minister

Environment Ontario
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POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS AND OTHER ORGANOCHLORINE CONTAMINANTS IN FOOD

PREPARED BY

THE JOINT OMAF/MOE
TOXICS IN FOOD STEERING COMMITTEE

AUGUST 1988

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EXECUTIVE SUMMARY

Public concerns were raised about the possible health hazards of toxic chemicals in Ontario food by the release of preliminary results from a study jointly funded by the Toronto Department of Public Health and the International Joint Commission, Toxic Substances Committee (Davies and Macpherson, 1986; Davies, 1988).

In May 1986, the Ministries of the Environment (MOE) and Agriculture and Food (OMAF) with technical assistance from Health and Welfare Canada (HWC) undertook a study of contaminants in food commodities produced or purchased in Ontario. The purpose of the study was to measure the levels of organochlorine residues in food with particular emphasis on polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzo furans (PCDF). The possible health significance of the residues was evaluated relative to established regulatory standards or tolerable or acceptable daily intakes. In the case of PCDD and PCDF the maximum allowable daily intake developed by MOE was used to evaluate possible health significance.

In Canada, HWC has the prime regulatory responsibility for establishing health-based food standards. Current regulations set by HWC under the Food and Drugs Act and Regulations (1986) do not allow PCDD in food. One exemption to this regulation allows up to 20 pg/g of 2,3,7,8-TCDD in fish. There are no current regulations for PCDF in food. HWC is expected to revise these regulations.

Study Design

Considerable effort went into the design of the study program in terms of choosing the appropriate food commodities and applying the necessary stringent quality assurance and quality control laboratory protocols to ensure that the analytical data were reliable. The major aspects of the study design are summarized below:

° Major food commodities commonly consumed by Ontario residents were identified. Six animal and six plant products were selected for analysis. The major sources (geographical location of the production) of these products available to the Ontario consumer were identified. The samples for analysis were collected from the major suppliers of these provincially-grown and imported foodstuffs.

° The selected foods were:

Animal Products
Prime beef steaks from Ontario and U.S.;
Hamburger beef from Ontario and New Zealand;
Pork chops from Western and Eastern Ontario and Quebec;
Broiler chickens from Ontario, Quebec and the U.S.;
Eggs (hen) from Western and Eastern Ontario and the U.S.; and
Milk (fresh, whole) from four regions of Ontario.

Plant Products
Apples from Ontario, B.C. and U.S.;
Peaches from Ontario and the U.S.;
Potatoes from Ontario, P.E.I. and the U.S.;
Tomatoes from Ontario and the U.S.;
Wheat from Ontario and Western Canada; and
Strawberries from Ontario and the U.S.

° The foods included in the analytical program are representative of those which are widely available to the consumer during the summer in Southern Ontario. These foods comprise the major foodstuffs consumed in the average diet.

- The food samples were analysed for the isomer-groups of PCDD and PCDF containing from four (4) to eight (8) chlorine atoms. These isomers are chemical compounds that are composed of the same atoms and have the same molecular formula, but differ in the way the chlorine atoms are arranged. These structural differences can greatly affect animal toxicity.

- In addition, all food commodities were analysed for twenty-five (25) other organochlorine pesticides and industrial organochlorine contaminants.

- The analytical program for PCDD and PCDF included extensive quality assurance/quality control procedures which are necessary for the measurement of extremely low levels of contamination found in these food products. (Section 3.2).

Major Findings

- PCDD and PCDF analyses of the plant products showed non-detectable residue levels of T_4CDD, P_5CDD, H_6CDD, and H_7CDD; T_4CDF, P_5CDF, H_6CDF, H_7CDF and O_8CDF. Very low levels of O_8CDD, (8 ppt or less) were found in U.S. peaches, and all wheat and potato samples.

- In the animal products, low levels of O_8CDD were found in some samples: all chicken and prime beef, U.S. eggs and Ontario hamburger. The other positive results were in U.S. eggs which had 5 to 12 pg/g (parts-per-trillion) of H_6CDF, H_7CDF, and O_8CDF; and 15 pg/g of H_7CDD in Quebec chicken. The analytical results of PCDD and PCDF are discussed in detail in Section 4.1.

- The analytical results of the agricultural and industrial organochlorine contaminants showed a small number of positive values, although residues were low ranging from 0.26 to 1 ng/g (parts per billion) (Section 4.2). No residues of PCB or mirex were detected. HCB residues when detected in B.C. apples, Ontario and New Zealand hamburger beef, and U.S. prime beef were below 1 ng/g. Pentachlorophenol residues were found in most food samples with values ranging from 0.2 to 4.8 ng/g. There were no detectable DDT residues in animal or plant products. The presence of only DDE residues indicates historical applications of DDT or possibly long-range atmospheric transport.

Conclusions

- Fruit and vegetable samples were substantially free of PCDD and PCDF residues, especially the more toxic tetra, penta and hexachlorinated forms. Animal products contained residues of PCDD and PCDF since these contaminants are lipophilic.

- Ontario grown plant and animal products had lower or comparable PCDD and PCDF residues than samples imported from other provinces or the U.S.A.

- Overall the residue levels of PCDD and PCDF found in the present study are consistent with recent Canadian, German and U.S. data and are significantly lower than values reported by Davies and MacPherson (1986).

- Based on the present study, the calculated daily intake of PCDD and PCDF from consumption of commercially available food in Ontario is 1.52 picogram of toxic equivalents (TEQ) per kg body weight per day, or 15% of the maximum allowable daily intake of 10 pg TEQ per kg body weight per day proposed by Ontario (MOE, 1985a). Animal products contribute 1.5 picograms TEQ per kg body weight per day or 99%, whereas plant products contribute 0.02 picograms of TEQ per kg body weight per day, or 1% of the total exposure.

° Compared to exposure estimates for other sources (air, water, soil, consumer products) food intake is the largest exposure pathway for the human receptor, accounting for 95% of the total intake of PCDD and PCDF.

° To provide a worse case estimate of intake via the food basket, exposure can also be calculated by assuming that PCDD and PCDF residues are present at the minimum detection levels reported in this study and elsewhere. Using these very conservative assumptions, total exposure via the food pathway is estimated at 2.28 pg of TEQ per kg body weight per day, or 23% of the maximum allowable daily intake.

° No residues of pesticides exceeded the maximum residue limits (MRL) as outlined in the Food and Drugs Act and Regulations (1986). In fact, the detected residues were one tenth to five hundredths of the Maximum Residue Limits (MRL).

° In the case of non-agricultural pesticides and industrial chemical contaminants, no residues of PCB, 2,4,5-trichlorophenol, or mirex were detected. Detectable residues of HCB, 2,3,4,6-tetrachlorophenol and pentachlorophenol were not considered significant in terms of risk to public health.

° Pentachlorophenol, a wood preservative, was found in all food samples, except Eastern Ontario eggs. The presence of low levels of H_6CDD, H_7CDD and O_8CDD in some foods may be related to the P_5CP residues.

- Residues levels of pesticide and other industrial contaminants reported in the present study are consistent with the findings of other OMAF, Canadian and U.S. monitoring studies and confirm the observed trend for declining residues of these compounds in food commodities.

SOMMAIRE

Les résultats préliminaires d'une étude financée conjointement par le Service de la santé publique de Toronto et la Commission mixte internationale (Comité des substances toxiques) soulèvent des inquiétudes chez la population concernant les dangers éventuels des produits chimiques toxiques que renferment les aliments en Ontario (Davies et Macpherson, 1986; Davies, 1988).

En mai 1986, le ministère de l'Environnement et le ministère de l'Agriculture et de l'Alimentation ont effectué, avec le concours technique de Santé et Bien-être social Canada, une étude sur les contaminants dans les denrées alimentaires produites ou achetées dans la province. L'étude avait pour but de mesurer les niveaux des résidus d'organochlorés dans les aliments, en particulier les polychlorodibenzoparadioxines (PCDD) et les polychlorodibenzofurannes (PCDF). Les dangers possibles des résidus pour la santé ont été évalués en fonction des normes établies ou des doses quotidiennes tolérables ou admissibles. Dans le cas des PCDD et des PCDF, la dose quotidienne admissible fixée par le ministère de l'Environnement a servi à évaluer ces risques.

C'est à Santé et Bien-être social Canada qu'il revient d'établir des normes de santé en ce qui concerne les aliments. En vertu des règlements pris en application de la Loi sur les aliments et drogues (1986), le ministère ne permet pas les PCDD dans ceux-ci. Une exception permet jusqu'à 20 parties par billion de 2,3,7,8-TCDD dans le poisson. Les règlements ne font aucune mention des PCDF, mais on s'attend que le ministère les révise.

Méthodologie de l'étude

On a mis beaucoup de soins à choisir les denrées alimentaires appropriées et à appliquer de rigoureuses normes d'assurance et de contrôle de la qualité en laboratoire pour faire en sorte que les données des analyses soient fiables. Les principaux aspects de l'étude sont résumés ci-après.

- Les principales denrées alimentaires couramment consommées par les résidents de l'Ontario ont été identifiées. Six produits animaux et six produits végétaux en vente dans la province ont été retenus aux fins d'analyse. Les principales sources de production ont été établies. Des échantillons ont été recueillis auprès des principaux fournisseurs de ces denrées produites ou importées dans la province.

- Les aliments choisis étaient les suivants :

  Produits animaux
  Bifteck de l'Ontario et des États-Unis;
  Boeuf haché de l'Ontario et de la Nouvelle-Zélande;
  Côtelettes de porc de l'ouest et de l'est de l'Ontario, et du Québec;
  Poulets à griller de l'Ontario, du Québec et des États-Unis;
  Oeufs (de poule) de l'ouest et de l'est de l'Ontario, et des États-Unis;
  Lait (frais, entier) de quatre régions de l'Ontario.

  Produits végétaux
  Pommes de l'Ontario, de la Colombie-Britannique et des États-Unis;
  Pêches de l'Ontario et des États-Unis;
  Pommes de terre de l'Ontario, de l'Île-du-Prince-Édouard et des États-Unis;
  Tomates de l'Ontario et des États-Unis;
  Blé de l'Ontario et de l'Ouest canadien;
  Fraises de l'Ontario et des États-Unis.

- Ces aliments sont représentatifs de ceux que peuvent facilement se procurer les consommateurs au cours de l'été dans le sud de l'Ontario. Ils constituent par ailleurs les principales denrées du régime alimentaire moyen.

- Les échantillons d'aliments ont été analysés en vue de déceler les groupes isomères de PCDD et de PCDF contenant de quatre (4) à huit (8) atomes de chlore. Ces isomères sont des composés chimiques qui sont constitués des mêmes atomes et ont les mêmes formules moléculaires, mais qui diffèrent dans la façon dont les atomes de chlore sont disposés. Ces variations structurales peuvent grandement influencer la toxicité sur les animaux.

- De plus, on a recherché dans toutes les denrées alimentaires vingt-cinq (25) autres pesticides organochlorés et polluants industriels organochlorés.

- Le programme de détection de PCDD et de PCDF comportait les méthodes approfondies d'assurance et de contrôle de la qualité qui sont nécessaires pour mesurer les niveaux extrêmement faibles de contamination qu'on retrouve dans ces denrées alimentaires. (Partie 3.2)

Principales constatations

- Les analyses des produits végétaux ont révélé des niveaux non décelables de résidus de T_4CDD, P_5CDD, H_6CDD et H_7CDD, T_4CDF, P_5CDF, H_6CDF, H_7CDF et O_8CDF. De très faibles quantités de O_8CDD (8 parties par billion ou moins) ont été trouvées dans les pêches des États-Unis et dans tous les échantillons de blé et de pommes de terre.

- Pour ce qui est des produits animaux, de faibles quantités de O_8CDD ont été trouvées dans certains échantillons : tous les poulets et les biftecks, les oeufs des États-Unis et le boeuf haché de l'Ontario. Les autres résultats positifs concernaient les oeufs des États-Unis, qui comptaient de 5 à 12 parties par billion de H_6CDF, H_7CDF et O_8CDF; et les poulets du Québec, qui comptaient 15 parties par billion de H_7CDD. Les résultats des analyses de détection de PCDD et de PCDF sont examinés en détail dans la partie 4.1.

o L'analyse des polluants organochlorés agricoles et industriels a révélé un petit nombre de valeurs positives, mais les quantités de résidus étaient faibles : de 0,26 à 1 partie par milliard (partie 4.2). Aucun résidu de BPC ni de mirex n'a été décelé. Les résidus de HCB qui ont été détectés dans les pommes de la Colombie-Britannique, le boeuf haché de l'Ontario et de la Nouvelle-Zélande ainsi que le bifteck des États-Unis s'élevaient à moins de 1 partie par milliard. Des résidus de pentachlorophénol ont été trouvés dans la plupart des échantillons d'aliments, dans une proportion allant de 0,2 à 4,8 parties par milliard. On n'a détecté aucun résidu de DDT dans les produits animaux ou végétaux. La présence de résidus de DDE seulement est l'indice d'applications antérieures de DDT ou peut-être de leur transport atmosphérique à longue distance.

Conclusions

o Les échantillons de fruits et légumes étaient dans une large mesure libres de résidus de PCDD et de PCDF, surtout en ce qui concerne les formes tétra, penta et hexachloro, les plus toxiques. Les produits animaux contenaient des résidus de PCDD et de PCDF, car ces contaminants sont lipophiles.

o Les produits végétaux et animaux provenant de l'Ontario présentaient des résidus de PCDD et de PCDF inférieurs ou comparables à ceux que renfermaient les échantillons importés d'autres provinces ou des États-Unis.

- Dans l'ensemble, les niveaux de résidus de PCDD et de PCDF qu'on a trouvés dans le cadre de la présente étude correspondent aux données de récentes études menées au Canada, en Allemagne et aux États-Unis, et sont sensiblement plus faibles que les valeurs signalées par Davies et MacPherson (1986).

- D'après la présente étude, la dose quotidienne de PCDD et de PCDF provenant de la consommation d'aliments en vente sur le marché ontarien s'élève à 1,52 picogramme d'équivalents toxiques par kilogramme de poids corporel par jour, soit 15 % de la dose quotidienne maximale admissible de 10 picogrammes d'équivalents toxiques par kilogramme de poids corporel par jour, dose proposée par le ministère de l'Environnement de l'Ontario en 1985. Les produits animaux contribuent 1,5 picogramme d'équivalents toxiques par kilogramme de poids corporel par jour, soit 99 % de la consommation totale, et les produits végétaux, 0,02 picogramme, ou 1 %.

- Comparativement à d'autres sources (air, eau, sol, produits de consommation), l'ingestion d'aliments est la principale source d'exposition aux PCDD et aux PCDF, intervenant pour 95 % de la consommation totale.

- Pour donner l'estimation la plus pessimiste de la consommation par le panier à provisions, on peut également calculer l'exposition en supposant que des résidus de PCDD et de PCDF sont présents aux niveaux minimums de détection qui sont signalés dans la présente étude et ailleurs. Par conséquent, on estime l'exposition totale par l'ingestion d'aliments à 2,28 picogrammes d'équivalents toxiques par kilogramme de poids corporel par jour, soit 23 % de la dose quotidienne maximale admissible.

- Aucun résidu de pesticides n'a excédé les limites maximales de résidus qui sont mentionnées dans la Loi et le Règlement sur les aliments et drogues (1986). En fait, les résidus détectés représentaient entre un dixième et cinq centièmes des limites maximales.

- Dans le cas des pesticides non agricoles et des polluants chimiques industriels, on n'a détecté aucun résidu de BPC, de 2,4,5-trichlorophénol ni de mirex. Les résidus de HCB, de 2,3,4,6-tétrachlorophénol et de pentachlorophénol n'ont pas été jugés significatifs en termes de dangers pour la santé publique.

- On a trouvé du pentachlorophénol, un préservatif du bois, dans tous les échantillons d'aliments, à l'exception des oeufs de l'est de l'Ontario. La présence de faibles quantités de H_6CDD, de H_7CDD et de O_8CDD dans certains aliments peut être liée aux résidus de P_5CP.

- Les niveaux des résidus de pesticides et d'autres polluants industriels qui sont signalés dans la présente étude correspondent aux constatations d'autres études effectuées par le ministère de l'Agriculture et de l'Alimentation, au Canada et aux États-Unis, et confirment les tendances à la baisse des résidus de ces composés dans les denrées alimentaires.

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Dr. John J. Ryan
Health Protection Branch

TERMS OF REFERENCE

1. To develop an analytical program to estabish baseline levels of organochlorine contaminants including polychlorinated biphenyls (PCB), polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in major foodstuffs available to Ontario consumers.

2. To ensure that the analytical work carried out under the program meets the stringent quality assurance/quality control criteria to allow confidence in the data.

3. To prepare a report on the scientific methods and findings of the studies.

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OMAF staff carried out all the analytical work on organochlorine contaminants other than PCDD and PCDF.

MOE laboratory staff (Drs. Vince Taguchi and Eric Reiner) performed the high resolution mass spectrometry analyses for PCDD and PCDF in selected samples, following the sample extraction and analytical work by the contract laboratory, Zenon Environmental Incorporated.

Special thanks are due to the staff of the Information Processing Centre, Hazardous Contaminants Coordination Branch, Ministry of the Environment for typing this document plus multiple earlier drafts. Their cooperation and professionalism has greatly helped in the production of the report.

ABBREVIATIONS

ADI	-	acceptable daily intake
BCF	-	bioconcentration factor
bw	-	body weight
2,4-D	-	2,4-dichlorophenoxyacetic acid
DDE	-	1,1-dichloro-2,2-bis (4-chlorophenyl) ethylene
fg	-	femtogram (10^{-15}g)
GC	-	gas chromatography
GC-MS	-	gas chromatography-mass spectrometry
GLC	-	gas-liquid chromatography
g	-	gram
H_6CDD	-	hexachlorodibenzo-p-dioxin
H_6CDF	-	hexachlorodibenzofuran
H_7CDD	-	heptachlorodibenzo-p-dioxin
H_7CDF	-	heptachlorodibenzofuran
HCB	-	hexachlorobenzene
HCH	-	hexachlorocyclohexane (gamma and beta isomers) (gamma HCH is Lindane)
HRGC	-	high resolution (capillary column) gas chromatography
HRMS	-	high resolution mass spectrometry
KL	-	kilolitre (10^3L)
kg	-	kilogram
L	-	litre
LRMS	-	low resolution mass spectrometry
MDL	-	minimum detection limit
MRL	-	maximum residue limit
MS	-	mass spectrometry
mg	-	milligram (10^{-3}g)
mL	-	millilitre (10^{-3}L)
ng	-	nanogram (10^{-9}g)
O_8CDD	-	octachlorodibenzo-p-dioxin
O_8CDF	-	octachlorodibenzofuran
o,p'-DDT	-	1,1,1-trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane
P_5CDD	-	pentachlorodibenzo-p-dioxin
P_5CDF	-	pentachlorodibenzofuran

P_5CP	- pentachlorophenol
PBB	- polybrominated biphenyl
PCB	- polychlorinated biphenyl
PCDD	- polychlorinated dibenzo-p-dioxin
PCDF	- polychlorinated dibenzofuran
pg	- picogram (10^{-12}g)
ppb	- parts per billion (10^{-9} g/g or ug/L)
ppm	- parts per million (10^{-6} g/g or mg/L)
ppq	- parts per quadrillion (10^{-15} g/g or pg/L)
ppt	- parts per trillion (10^{-12} g/g or ng/L)
p,p'-DDT	- 1,1,1-trichloro-2,2-bis (4-chlorophenyl) ethane
sub-ppt	- below 1 part per trillion
2,3,7,8-TCDD	- 2,3,7,8-tetrachlorodibenzo-p-dioxin
2,4,5-T	- 2,4-5-trichlorophenoxyacetic acid
T_3CP	- trichlorophenol
T_4CDD	- tetrachlorodibenzo-p-dioxin
T_4CDF	- tetrachlorodibenzofuran
T_4CP	- tetrachlorophenol
TDE	- 1,1-dichloro-2,2-bis (p-chlorophenyl) ethane
TEF	- toxicity equivalency factor
TEQ	- toxic equivalents
tonne	- 10^3 kilogram
ug	- microgram (10^{-6}g)
uL	- microlitre (10^{-6}L)

1.0 INTRODUCTION

Public concerns were raised about the possible health hazards of toxic chemicals in Ontario food by the release of preliminary results from a study jointly funded by the Toronto Department of Public Health and the International Joint Commission, Toxic Substances Committee (Davies and Macpherson, 1986; Davies, 1988).

Analyses of pesticides and industrial organochlorine contaminants in food have been carried out by Health & Welfare Canada federally and the Ontario Ministry of Agriculture & Food provincially for a number of years. However, food has only recently been investigated as a potential source of PCDD and PCDF. Due to the extremely expensive and difficult analytical procedures required, limited data are available on baseline levels of PCDD and PCDF in food.

Under the Food and Drugs Act and Regulations, Health & Welfare Canada has the responsibility and also has the required analytical capability to analyse for a variety of contaminants in food including PCDD and PCDF. To date, Health & Welfare Canada have been determining PCDD and PCDF in foods such as freshwater fish and those known to be contaminated by chlorophenolic residues.

A joint technical committee of staff from the Ontario Ministries of Agriculture and Food (OMAF) and Environment (MOE), with technical advice from Health & Welfare Canada, was formed in May 1986 to develop and oversee an analytical program for organochlorine contaminants, including polychlorinated biphenyls (PCB), polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in the major foodstuffs available to Ontario consumers.

PCDD and PCDF analyses were performed by Zenon Environmental Inc., the successful contractor on the tendered program. Additional analyses by high resolution gas chromatography - mass spectrometry (GC-MS) to lower the detection limits of PCDD and PCDF were carried out at the Ministry of the Environment laboratories as the contractor did not have this capability. Analyses for the other organochlorine contaminants were performed by the Ministry of Agriculture and Food Pesticides Laboratory. The quality assurance/quality control protocols developed for use in this study are summarized in Section 3.2.

The rationale for the selection of food and details of the sample collection are described in Section 2 and Appendix A. The main criterion for food selection and sampling was to maximize the match between the food product availability and the average dietary consumption patterns in Ontario.

1.1 Background to Organochlorine Contaminants in Food Study

Organochlorine contaminants include older chlorinated pesticides, many of which have been removed from use, and industrial pollutants such as PCB, PCDD and PCDF. These contaminants are most frequently observed in meat, fish, poultry, oils and other foods of high lipid content because of their "lipophilic" nature, that is, their high affinity for fats.

1.1.1 Residues of PCDD and PCDF in Food

Human exposure to PCDD and PCDF may occur occupationally, accidentally, from dietary intake, or from environmental exposure to air, water or soil. The persistent and bioaccumulative properties of PCDD and PCDF suggest that these pollutants may enter the food chain and contaminate the human diet.

Recent reports (Ryan et al., 1985b,c); Graham, et al., 1985) on 2,3,7,8-TCDD and a variety of other PCDD and PCDF in adipose tissue of Canadian and U.S. residents indicate widespread low level exposure to these chemicals.

PCDD and PCDF can enter the environment and subsequently the diet in a variety of ways; e.g. as contaminants in the production and use of chlorophenol-based chemical products, as products of combustion and as components of solid, liquid and airborne wastes and emissions. The presence of 2,3,7,8-TCDD in the environment is primarily associated with the past production and use of 2,4,5-trichlorophenol-based chemical products and at lower concentrations from incineration processes.

The presence of more highly chlorinated PCDD and PCDF in the environment can be related to the use of chlorophenol-based wood preservatives. A variety of PCDD and PCDF are found in the emissions from industrial, municipal and domestic incineration processes to generate power and heat and reduce wastes. In urban areas, motor vehicle emissions may also contribute to combustion emissions. Recently PCDD and PCDF have been found in effluents and products of the pulp and paper industry.

2,3,7,8-TCDD residues were first reported in fish from the Great Lakes region. The MOE Sportfish monitoring program has an extensive component devoted to analysing fish samples from the Great Lakes, inter-connecting waterways and some tributary streams (MOE, 1985a, 1986b). In addition, the federal government has carried out two surveys of commercial fish taken from Ontario waters (Ryan et al., 1984; Ryan et al., unpublished).

Fish monitoring programs indicate that 2,3,7,8-TCDD is occasionally detected in samples from the Niagara River, Lake Ontario and some northern locations near pulp mills (MOE, 1985b, 1986b). Residues of 2,3,7,8-TCDD in the edible portion of these fish when detected rarely exceed 20 ppt, the food consumption guideline permitted by the Food and Drugs Act and Regulations (1986).

Data from recent U.S. and Canadian studies indicate that some Great Lakes fish contain very low levels (parts-per-trillion) of other PCDD and PCDF. Higher chlorinated PCDD and PCDF are not generally detected. Consequently, fish are probably not a source of higher chlorinated PCDD and PCDF to man (MOE, 1985a).

1.1.2 Monitoring Studies of PCDD and PCDF in Food

Historical reports on the presence of PCDD and PCDF in domestic animals and food commodities other than fish as related to human diet have been quite limited (NRCC, 1981).

Most of these data were obtained from areas around Seveso, Italy, site of a major industrial accident that released 2,3,7,8-TCDD. Other U.S. and Canadian data have been obtained from poisoning episodes in cattle, swine or chickens involving contaminated animal feed, contaminated animal bedding or chemically treated farm structures. These studies have implicated pentachlorophenol as the main source since most samples contained measurable amounts of pentachlorophenol and only trace levels of H_6CDD, H_7CDD and O_8CDD.

Recently, some governments have initiated monitoring of PCDD and PCDF residues as part of established total diet programs or market basket surveys (Firestone et al., 1985b; Mathar et al., 1987; Ono et al., 1987; HWC unpublished, Appendix B of this report).

These studies indicate that T_4CDD, T_4CDF, P_5CDD and P_5CDF were not detected or are present at sub-ppt levels in cow's milk, meat, poultry and eggs. H_6CDD, H_6CDF, H_7CDD, H_7CDF, O_8CDD and O_8CDF were not detected or are present in low ppt levels, e.g. generally <5 to 25 ppt. However O_8CDD may be found in excess of 200 ppt in some samples.

Fruit and vegetable samples tend to have substantially lower residue levels than milk, eggs or meats, generally in the sub-ppt range. For example, the German federal study could not detect PCDD or PCDF in apples, cherries, salad, cauliflower or vegetable oil at the 0.02 ppt level of detection (Mathar et al., 1987).

By contrast, the study of Davies and Macpherson (1986) reported highest levels of PCDD and PCDF in their fruit sample, up to 6600 ppt (Table 5.1). They also found some measurable levels of PCDD and PCDF in samples of vegetables, milk and meat/eggs with a high value of 120 ppt of T_4CDF in milk.

1.1.3 Pesticide Residues in Food

Several persistent and bioaccumulative pesticides were restricted from agricultural use in Ontario in the late 1960s and early 1970s. These include DDT, TDE, aldrin, dieldrin, endrin and heptachlor while less persistent compounds like chlordane and toxaphene were removed from agricultural uses later in the 1970s. Others, like endosulfan and methoxychlor are still used in small quantities.

Many screening programs for pesticide residues include these compounds and their metabolites and they are often reported as "pesticides". More correctly, they should be classified as "contaminants" to distinguish them from pesticide residues arising from the intentional use of registered pesticides in the production of food products.

Few pesticides currently used in the production of foods are detected in the final food product by the time it gets to market. The pesticide residues that do appear are those that are directly applied to fruit and vegetables late in the season. However, detected residues rarely exceed the maximum residue limit (FRMCP, 1985).

Persistent contaminant residues from past uses tend to be higher on root or underground crops, whereas currently used pesticides, when present, tend to be found on leafy vegetables, and on fruit treated close to harvest where the residue serves as a post-harvest control to prevent storage rots or decays.

Some contaminant residues, like DDE and PCB tend to be ubiquitous in lipid materials. However, most investigations confirm that over the last 10-15 years since their removal from use, a significant decline in residues has occurred and negligible residue levels are now being approached (See Appendix E).

With the removal of the major persistent organochlorine insecticides during the period 1969-78, a marked decline has been observed in the residues of both parent materials and metabolities in all food commodities. Residue levels in most foods are now below detection limits and in some cases, have been for the last few years. Only occasional foods of animal origin are found with trace levels of these substances. This decline is also true for PCB, an industrial contaminant banned from open uses in 1977.

1.1.4 Monitoring Studies of Pesticides in Food

(i) Canada: The Food Residue Monitoring Consolidation Program (FRMCP), coordinated by the Pesticides Directorate, Agriculture

Canada, consolidates and publishes pesticide residue data from Canadian food monitoring programs (FRMCP, 1985). Only Canadian-grown produce is included and the residue data are from routine monitoring programs. Generally, the food was fresh, not processed, and samples were randomly selected. Residue data were compiled from analytical results from 10 Federal and Provincial agencies. Table 1.1 summarizes the data for 1985.

(ii) Ontario - OMAF Studies: The Agricultural Laboratory Services Branch, OMAF, has an on-going monitoring and surveillance program to determine pesticides and industrial pollutants in Ontario-produced foodstuffs as they are shipped to market (Frank et al., 1987a,b). The results from these surveys agree with residues observed by other Canadian and U.S. researchers (FRCMP, 1985; Gartrell et al., 1985a,b,c,d; 1986a,b). A review of Ontario-OMAF studies is found in Appendix E.

(iii) Ontario - Davies and Macpherson Report 1986: The Davies and Macpherson report (1986) presented results on organochlorines, PCB, PCDD and PCDF residues in food and their contribution to human exposure.

In their report, they analysed "composites of fresh foods grown in Southern Ontario and purchased in Toronto supermarkets". The food composites represented the following five groups: fresh meat and eggs; root vegetables including potatoes; fresh fruit; leafy and other above ground vegetables; and cow's milk. However, it is not clear whether their data, reproduced as Table 5.4, were from wholly Ontario produced foodstuffs.

TABLE 1.1 : SUMMARY OF PESTICIDE RESIDUES FOUND IN CANADIAN GROWN FOODS IN 1985 (ADAPTED FROM FRMCP, 1985)

	FOODSTUFF							
	Fruit	Vegetables	Meat	Grain	Eggs	Feed	Milk and Products	Total
Number of food commodities examined	10	9	9	9	1	1	3	35
Number of pesticides analyzed	109	115	32	35	22	47	48	155
Number of samples	910	447	261	324	163	341	456	2702
Number of samples with detectable residues	121	123	155	162	4	56	401	1022
Percent of samples in compliance with MRL	99.0	98.2	100	99.6	100	*	100	99.34

* No MRL

Their conclusion was that although a wide variety of organochlorine residues were detected in all the composite samples, all concentrations were below the Canadian MRLs. Finally, they concluded that their data "suggested that fresh food grown in Southern Ontario is no more and no less contaminated with (pesticide) residues than foods grown in the U.S.".

2.0 STUDY PLAN

The joint OMAF/MOE Committee reviewed the Davies & Macpherson (1986) report and concluded that many of the food items listed as produced in Ontario were, in fact, imported and repacked for sale. At the same time, wide differences in PCDD and PCDF levels were noted between summer and winter collections. The committee had access to other data on these contaminants in food from the Health Protection Branch, Health & Welfare Canada (Appendix B) and from MOE analysis of apples and milk (Appendix C), that were at variance with these findings. The committee decided that in the present study the major thrust should be to monitor Ontario-produced food and major imports.

The work plan was divided into three phases: Phase I was designed to validate the comparability of the various methods used for analysing PCDD and PCDF in plant tissues since no standard method was being used by the laboratories doing the analysis. Phase II was designed to analyse the major food commodities for PCDD and PCDF, as well as other organochlorine pesticides and contaminants. Phase III was optional and was designed as a follow up to Phase II for the investigation of those foods where unacceptable levels of residues were found.

Based on the results from Phase II, the Committee determined that Phase III was not necessary as part of this study.

Phase II was the major component of the study and included:

(1) selecting specific foods for analysis based principally on the average consumption patterns of Ontario residents; and
(2) where possible, comparing Ontario produce with the same food item grown outside the Province.

2.1 Selection of Food Commodities

Food commodities for analysis were selected on the basis of average consumption patterns for Ontario residents. Also, where possible, the same food items produced outside of Ontario were analysed for comparative purposes

The Canadian dietary figures from two sources were reviewed (Smith, 1971, Food Processors Survey, unpublished). In addition, an estimate was made of the per capita consumption based on domestic production, minus exports but including imports. The quantities from these sources appear in Appendix A (Tables A.1 to A.3). Six major animal and six major plant commodities that were readily available in June to August were selected (Tables 2.1 and 2.2). Raw milk samples as a part of this study had previously been selected and analysed in May 1986.

In order to determine the origin of these twelve food items, the Ontario production figures were prepared giving exports and imports (Table A.3). These tradings in food commodities occur because Ontario production is seasonal and at certain times of the year there are surpluses to be exported while at other times there are short-falls and imports are needed. In considering whether domestic or imported foods should be sampled, the major sources of supply of each of the twelve commodities were reviewed for the months of June to August.

The focus on sampling the June to August period was based on the suggestions from the Davies and Macpherson (1986) report that the high PCDD and PCDF levels found by them were due to airborne sources of contamination in the Great Lakes Basin. In particular, incineration sources were suggested as the major origin. Therefore this sampling period should provide Ontario commodities that have maximum exposure to airborne contaminants.

A third point for consideration was the variety and package of food commodity to select, and the cut in the case of meats. Consumers purchase foods in many different forms and packages: for example, beef can be obtained as steaks, hamburger, roasts, etc. Hence the most common forms offered to the consumer were selected.

A final consideration in the selection of the food samples was to include those commodities that the Davies & Macpherson Report (1986) indicated were contaminated with PCDD and PCDF.

In summary the following criteria were used to select food commodities for sampling:

(1) Six should be of animal and six of plant origin.
(2) Major food items available in June to August be chosen.
(3) The major package item be selected.
(4) The major sources of supply be used.
(5) Select foods reported to be contaminated.

As a result of these considerations, the committee arrived at the list of food items in Tables 2.1 and 2.2 as the commodities to be sampled for analysis.

As described in Tables 2.1 and 2.2 a total of twelve commodities that ranked as major or primary raw food items for the Ontario consuming public were selected for analysis. Samples were purchased by OMAF. Six animal products and six plant products were included. The animal products included raw milk that had been sampled and analysed just prior to commencement of the main study.

The details of the collection methods and origins of the food commodities are found in Appendix A.

TABLE 2.1 : LIST OF ANIMAL PRODUCTS SELECTED FOR SAMPLING OVER THE JUNE-AUGUST PERIOD AND THEIR ORIGINS

COMMODITY	SOURCE	% ONTARIO CONSUMPTION BY SOURCE DURING SAMPLING PERIOD	TOTAL %
Beef-Prime steaks	U.S.	6	
-Prime steaks	Ontario)		
	)	84	92
Beef-hamburger	Ontario)		
-hamburger	New Zealand	2	
Pork-chops	W. Ontario	65	
	E. Ontario	25	100
	Quebec	10	
Chicken-whole broiler	Ontario	83	
	Quebec	4	100
	U.S.	13	
Eggs-hen	W. Ontario	57	
	E. Ontario	40	100
	U.S.	3	
Milk-fresh whole	W. Ontario	32	
	C. Ontario	14	
	E. Ontario	27	78
	N. Ontario	5	
	S.W. Ontario	not sampled	

TABLE 2.2 : LIST OF PLANT PRODUCTS SELECTED FOR SAMPLING OVER THE JUNE-AUGUST PERIOD AND THEIR ORIGINS

COMMODITY	SOURCE	% ONTARIO CONSUMPTION BY SOURCE DURING SAMPLING PERIOD	TOTAL %
Apples-fresh	Ontario	58	
	New York	18	100
	Pacific coast	24	
Peaches-fresh	Ontario	40	
	U.S.	44	84
Potatoes	Ontario	50	
	U.S.	8	100
	P.E.I.	42	
Strawberries	Ontario	41	
	U.S.	53	94
Tomatoes	Ontario	80	
	U.S.	18	98
Wheat	Ontario	47	
	W. Canada	53	100

3.0 ANALYTICAL PROCEDURES

3.1 Sample Preparation and Storage

All sampling was performed by staff of the Ontario Ministry of Agriculture & Food as described in Appendix A.

Raw samples were delivered to the Ontario Ministry of the Environment, Laboratory Services Branch, Dioxin Analysis Facility in Rexdale, Ontario for processing. Seven replicates of each sample were prepared, each having a sample size of 100 g (wet weight). After samples were prepared, they were stored in a freezer at -10°C until delivery to the analytical laboratories. Frozen samples were hand-delivered to laboratories within a few hours of removing from storage.

To ensure that food samples were not contaminated by chemical residues in the laboratory processing, a number of pre-cleaning and handling steps were followed. The detailed description of these procedures is found in Appendix A.

3.2 Sample Extraction and Analysis: PCDD and PCDF

The analysis of food samples for PCDD and PCDF was performed under contract by Zenon Environmental Inc., the same laboratory that analysed food samples in a previous supermarket food-basket study (Davies and Macpherson, 1986).

Since only a validated analytical methodology was to be used in the current study, it was specified in the contract that the methods developed by Health & Welfare Canada for the analysis of food for PCDD and

PCDF must be followed. However, it was also an objective of this work to compare the method used by the Contractor in their previous food basket work with the method used by Health & Welfare Canada for analysis of fruits and vegetables. Method comparison for these food groups was important due to the previous finding by the Contractor of significant levels of total PCDD and PCDF in a single fruit composite sample. Since that fruit composite contained over 60% apples by weight, the method comparison was performed using a composite of Ontario apples that was prepared as described in Appendix A.

3.2.1 Phase I: Method Comparison for PCDD and PCDF in Apples

The work for Phase I of this study was completed before beginning the Phase II work, and is described in detail in a previous report (Zenon Environmental Inc., 1987).

Results of the Phase I study, shown in Table 3.1, demonstrated that the Contractor's existing methodology for PCDD and PCDF in apples produced results comparable to those generated by the Health & Welfare Canada method.

Therefore the Contractor used their existing methodology for extraction and analysis of fruit and vegetable samples. However, the extraction method used by Health & Welfare Canada was employed for analysis of the animal product samples.

3.2.2 Phase II: Analysis of Food for PCDD/PCDF

The Contractor received frozen food homogenates from MOE, which were assigned internal laboratory identification numbers and stored frozen until analysis. Samples were extracted in two batches.

TABLE 3.1 : COMPARISON OF METHODOLOGIES FOR ANALYSIS OF APPLES FOR PCDD AND PCDF
(All data parts-per-trillion: ppt)

	ZENON ENVIRONMENTAL METHOD				HEALTH & WELFARE CANADA METHOD			
PCDD	Blank	S1[2]	S2	S3	Blank	S4	S5	S6
T_4CDD	ND(1)[1]	ND(1)	ND(1)	ND(1)	ND(1)	ND(1)	ND(1)	ND(1)
P_5CDD	ND(6)	ND(6)	ND(6)	ND(6)	ND(2)	ND(2)	ND(2)	ND(2)
H_6CDD	ND(10)	ND(10)	ND(10)	ND(10)	ND(6)	ND(6)	ND(6)	ND(6)
H_7CDD	ND(7.5)	ND(7.5)	ND(7.5)	ND(7.5)	ND(15)	ND(15)	ND(15)	ND(15)
O_8CDD	ND(5)	ND(5)	ND(5)	ND(5)	ND(7.5)	ND(7.5)	ND(7.5)	ND(7.5)
PCDF								
T_4CDF	ND(1)	ND(1)	ND(1)	ND(1)	ND(1)	ND(1)	ND(1)	ND(1)
P_5CDF	ND(6)	ND(6)	ND(6)	ND(6)	ND(2)	ND(2)	ND(2)	ND(2)
H_6CDF	ND(12)	ND(12)	ND(12)	ND(12)	ND(6.5)	ND(6.5)	ND(6.5)	ND(6.5)
H_7CDF	ND(7.5)	ND(7.5)	ND(7.5)	ND(7.5)	ND(15)	ND(15)	ND(15)	ND(15)
O_8CDF	ND(5)	ND(5)	ND(5)	ND(5)	ND(7.5)	ND(7.5)	ND(7.5)	ND(7.5)
% Recoveries								
T_4CDD	24	47	26	53	75	39	25	35
O_8CDD	56	77	38	98	84	46	27	26

---

[1] ND - not detected, detection limits given in brackets (ppt)

[2] S1 to S6 - apple samples 1 to 6

The animal product samples were extracted and analysed first, followed by the samples of fruits and vegetables.

PCDD/PCDF Analysis by Contractor

In previous analytical programs, problems have occurred because of contamination in the analytical process. Extensive quality control measures were incorporated into this investigation. They are summarized below:

i) All sample preparation and extraction/ cleanup equipment was proven free of contaminants before using by GC-MS analysis of solvent rinsings of the equipment.

ii) All samples for PCDD and PCDF determination were sent to the Contractor as blind duplicates.

iii) All sample extraction glassware and conical vials for final extract storage were purchased new for this investigation.

iv) Detailed instructions were provided to the Contractor regarding analytical protocols and data reporting including the surrogate spiking levels to be used, GC-MS sensitivity required, determination of peak areas by manually setting peak baselines, criteria for positive responses, method of quantitation and surrogate recovery control limits, reporting of detection limits, and analysis of procedure blanks. In addition, the Contractor was required to supply printouts of raw data to MOE experts for their examination.

v) All samples were spiked with ^{13}C-T_4CDD and ^{13}C-O_8CDD before extraction to determine the efficiency of sample preparation procedures.

vi) An initial method comparison study was performed to validate the extraction procedure employed by the Contractor for fruit and vegetable samples.

vii) A procedure blank was analysed for each group of samples (approx. 1 blank per 6 samples).

viii) Samples were analyzed by HRGC-HRMS (nominal resolution 10,000).

ix) In-lab duplicates and sample re-injections were analysed by the Contractor.

x) Detailed data interpretation criteria were developed to ensure high reliability could be attached to the detection of PCDD/PCDF in sample extracts. These criteria incorporated accepted standard procedures for identification of PCDD/PCDF peaks by GC-MS in addition to the results of procedure blanks and replicate determinations.

xi) Stored replicates were available to confirm any significant finding of PCDD/PCDF by inter-laboratory comparative analysis.

A detailed description of the extraction, cleanup and analytical procedures for PCDD and PCDF employed by the contract laboratory is found in Appendix A.

Contamination Problems at Contract Laboratory

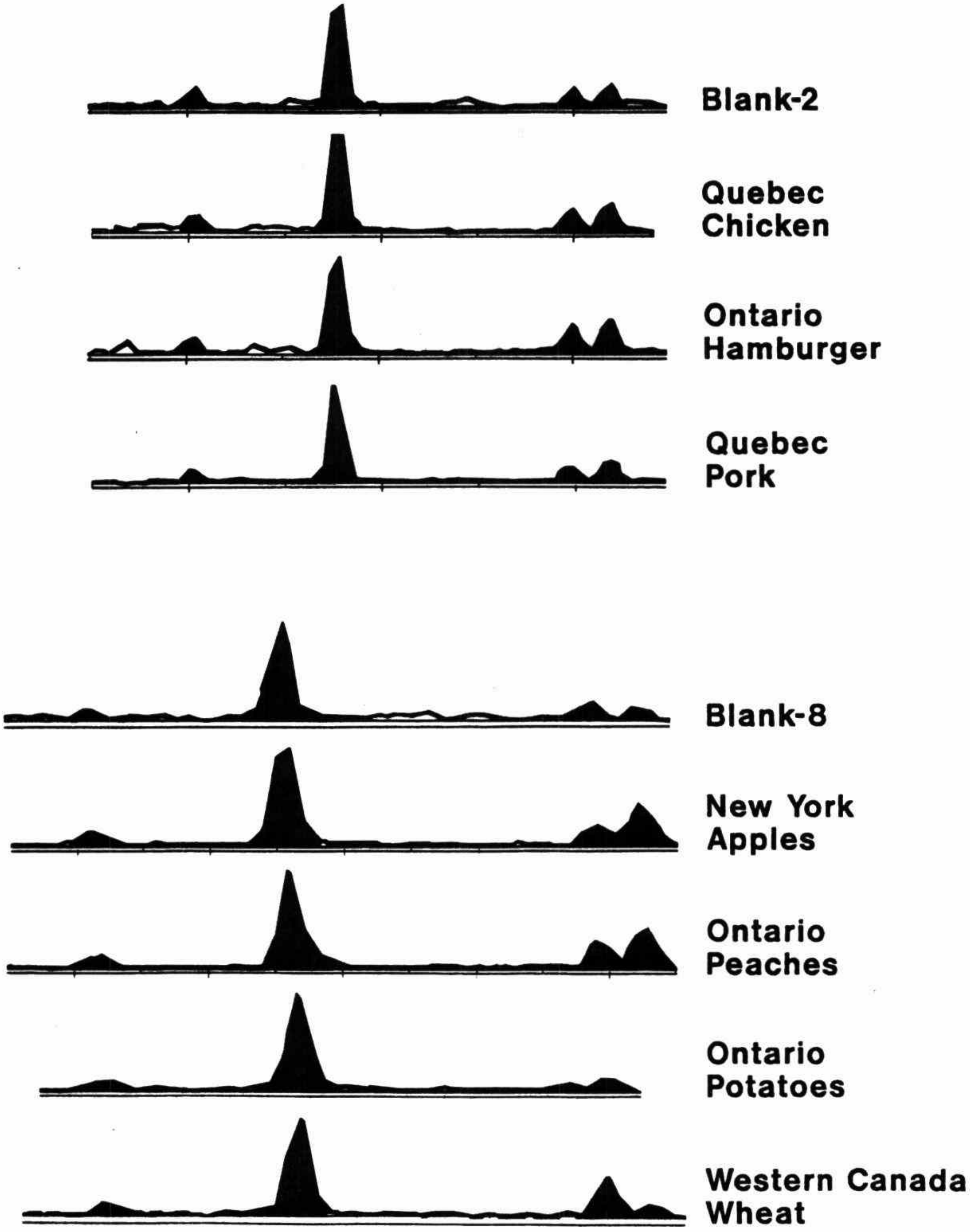
In the initial set of results supplied by the contractor, low levels of T_4CDF and P_5CDF were reported in many of the animal product samples. These congeners were also detected in some of the procedure blanks at lower concentrations. Examination of the raw GC-MS printouts showed that the same patterns of peaks were observed in the procedure blanks as for the samples.

Figure 3.1 shows the pattern of T_4CDF observed for several of the samples and procedure blanks. The similarity of these patterns in such widely varying food types and in the procedure blanks was overwhelming evidence that an internal source of laboratory contamination existed.

Detailed investigation by the contractor revealed the apparent T_4CDF and P_5CDF detected were actually chlorinated diphenyl ethers, a contaminant that exhibits mass spectral properties similar to those of the PCDF. These PCDF interferences are generally removed during sample cleanup. However, since they were also detected in the procedure blanks, it is probable that the contamination was introduced in the contractor's laboratory at some point after sample cleanup.

To remove the chlorinated diphenyl ether contaminants from sample extracts, an additional cleanup was performed by the contractor. All animal product extracts and one-half of the fruit and vegetable sample extracts were reprocessed. The additional cleanup consisted of column chromatography using a column of basic alumina. Re-analysis by GC-MS showed that this procedure was successful in removing the contaminants. Samples were also spiked with $^{13}C-T_4CDF$ before cleanup to monitor recoveries through the additional cleanup.

FIGURE 3.1 : APPARENT T_4CDF ISOMER PATTERNS IN BLANKS AND FOOD SAMPLES



Additional PCDD/PCDF Analysis by MOE

The additional cleanup to remove interferences and the necessity of making several injections of each sample during the course of this work contributed to average detection limits that ranged from about 5 ppt (T_4CDD/T_4CDF) to 30 ppt (O_8CDD/O_8CDF) for the LR-MS analyses by the contractor. In addition, interfering peaks in the animal product samples resulted in an average detection limit of 1100 ppt for the hexachlorinated dibenzofurans (H_6CDF) while interferences in the fruit and vegetable samples resulted in an average detection limit of 5,000,000 ppt for the heptachlorinated dibenzofurans (H_7CDF).

To eliminate the interferences, all samples were re-analysed by HRGC-HRMS (nominal resolution 10,000) at the MOE mass spectrometry laboratory in Rexdale. Details of the analysis of PCDD and PCDF by this technique are given in a recent publication (Taguchi *et al.*, 1988).

3.2.3 PCDD/PCDF Data Interpretation Criteria

All data were interpreted using a strict set of criteria designed to eliminate false positive results and ensure a high reliability of quantitation of PCDD and PCDF congeners.

Quantitation data for samples where blank contamination was found, where recoveries were outside expected values or where results could not be replicated are considered suspect and are not reported without explanation. The detailed criteria used are given in Appendix D.

3.3 Sample Extraction and Analysis: Organochlorine Insecticides and Industrial Chemicals

Frozen composite samples were delivered for analysis by courier from Ontario Ministry of the Environment to the OMAF Pesticide Laboratory on November 7, 1986 and January 6, 1987. The samples were held frozen until extraction within one week of delivery.

Of the seven replicates prepared for each sample, two were given different numbers and were shipped to the dioxin analysis contractor as blind duplicates; one was delivered to OMAF for determination of organochlorine insecticides and industrial chemicals, while three were retained for possible follow-up analysis.

The detailed extraction and analysis methods are found in Appendix A. The methods used are routine standard procedures employed by the OMAF laboratory in its regular on-going monitoring programs of foods.

Analytical recoveries were periodically confirmed as part of an on-going QA/QC program. Duplicate field samples and internal laboratory checks were also analysed at random. Fortification levels ranged from the detection limit of the procedure to greater than the maximum residue limit (MRL) for each contaminant as established under Food and Drugs Act and Regulations (1986).

Detection limits (Tables 4.5, 4.6, 4.7 and 4.8) represent the lowest limit to which the individual procedure was reproducible. These varied somewhat depending on the particular instrumentation employed and the substrate being analyzed.

Confirmation techniques were applied when residues were high enough to allow alternative procedures to be used. These included:

(i) the use of alternate-column GLC, for example using column packings of different polarity so that characteristic retention times were significantly changed, or

(ii) with a capillary gas chromatograph and mass selective detector using either full scan or single- or multiple-ion monitoring. Residue results are uncorrected for recoveries.

4.0 RESULTS

4.1 PCDD and PCDF

The results for 25 of the 26 food composite samples are shown in Tables 4.1 to 4.4. Results of the Phase I study on apples are found in Table 3.1. No data are shown for strawberries as these samples were lost due to improper storage (see Appendix A.2.1.2(x)). All data are in units of pg/g, (part per trillion).

4.1.1 Eggs

No detectable residues of PCDF were found in Ontario eggs (Table 4.1). Very low levels (less than 25 ppt) of O_8CDD, H_6CDF, H_7CDF, and O_8CDF were found in U.S. eggs.

Out of a total of 30 analytical determinations of the 10 isomer groups in egg samples, 25 were non-detectable (83%).

4.1.2 Meat

Very low levels (3 to 24 ppt) of O_8CDD were found in all prime beef and hamburger samples (Table 4.1) Out of a total of 40 analytical determinations of the 10 isomer groups in beef and hamburger samples, 37 were non-detectable (93%).

TABLE 4.1 : RESIDUES OF PCDD AND PCDF IN EGG AND BEEF SAMPLES*

	EGGS			PRIME BEEF		HAMBURGER	
	Western Ontario	Eastern** Ontario	U.S.A.	Ontario	U.S.A.	Ontario	New Zealand
T_4CDD	ND(4)	ND(1)	ND(4)	ND(2)	ND(4)	ND(2)	ND(2)
P_5CDD	ND(4)	ND(1)	ND(3)	ND(1)	ND(3)	ND(1)	ND(1)
H_6CDD	ND(4)	ND(1)	ND(2)	ND(1)	ND(1)	ND(1)	ND(3)
H_7CDD	ND(5)	ND(1)	ND(1)	NR(1)	ND(3)	ND(2)	ND(1)
O_8CDD	ND(6)	3(1)	8	12	24	3(2)	NR(6)
Total:	ND	ND	8	12	24	3	ND
T_4CDF	ND(9)	ND(2)	ND(4)	ND(2)	ND(1)	ND(1)	ND(2)
P_5CDF	ND(4)	ND(1)	ND(6)	ND(1)	ND(2)	ND(1)	ND(1)
H_6CDF	ND(5)	ND(1)	5^1	ND(1)	ND(1)	ND(1)	ND(1)
H_7CDF	ND(6)	ND(1)	7^3	ND(1)	ND(1)	ND(1)	ND(1)
O_8CDF	ND(6)	ND(1)	12	ND(1)	ND(2)	ND(1)	ND(2)
Total:	ND	ND	24	ND	ND	ND	ND

* All data in pg/g, parts per trillion, corrected for spike recovery. Concentration value followed by the detection limit in brackets if it is within three times the detection limit.

** Single determination only, all other data are averages of two replicate determinations

ND: Not detected at detection limit given in brackets (ppt)

NR: Not replicated. Value in brackets was determined in one replicate only.

Superscripts indicate number of peaks found in each isomer group.

TABLE 4.2 : RESIDUES OF PCDD AND PCDF IN PORK AND CHICKEN SAMPLES*

	PORK			CHICKEN		
	Eastern Ontario	Western Ontario	Quebec	Ontario	Quebec	U.S.A.
T$_4$CDD	ND(6)	ND(2)	ND(7)	ND(4)	ND(3)	ND(6)
P$_5$CDD	ND(6)	ND(3)	ND(4)	ND(3)	ND(2)	ND(3)
H$_6$CDD	ND(6)	ND(4)	ND(6)	ND(3)	ND(2)	ND(2)
H$_7$CDD	ND(2)	ND(2)	ND(3)	NR(2)	15^3	ND(2)
O$_8$CDD	ND(15)	ND(6)	ND(5)	17	210	26
Total:	ND	ND	ND	17	225	26
T$_4$CDF	ND(4)	ND(3)	ND(5)	ND(3)	ND(2)	ND(6)
P$_5$CDF	ND(4)	ND(2)	ND(5)	ND(3)	ND(2)	ND(3)
H$_6$CDF	ND(4)	ND(3)	ND(4)	ND(2)	ND(1)	ND(1)
H$_7$CDF	ND(3)	ND(2)	ND(4)	ND(2)	ND(1)	ND(1)
O$_8$CDF	ND(2)	ND(2)	ND(5)	ND(2)	ND(2)	ND(2)
Total:	ND	ND	ND	ND	ND	ND

* : All data in pg/g, parts per trillion, corrected for spike recovery. Data are averages of two replicate determinations

ND: Not detected at detection limit given in brackets (ppt)

NR: Not replicated. Value in brackets was determined in one replicate only.

Superscripts indicate number of peaks found in each isomer group.

Chicken samples also contained low levels of O_8CDD (17 to 26 ppt), except in the case of the Quebec sample where levels of O_8CDD were higher (210 ppt) and low levels of H_7CDD were also present. Pork samples did not contain residues at the detection level (Table 4.2).

Thirty (30) analytical determinations of the 10 isomer groups for each of 3 chicken and 3 pork samples are reported. All of the pork samples (100%) were non-detectable results. In the chicken samples, 26 were non-detectable (87%).

4.1.3 Fruit

Except for very low levels of O_8CDD (8 ppt) in the New York sample, no residues were found in apples at the very low levels of detection (Tables 3.1 and 4.3). A sub-ppt level of O_8CDD (0.6 ppt) was found in the U.S. peach sample. No residues were found in Ontario peaches. (Table 4.4).

A total of 30 analytical determinations of the 10 isomer groups for apples are reported in Phase II. Of these, 29 are non- detectable results (97%). In Phase I (Table 3.1), 100% of the reported results were non-detectable. In both Phase I and Phase II, 100% of the results from Ontario apples were non-detectable.

Twenty (20) analytical determinations of the 10 isomer groups are reported for peaches, 19 of which are non-detectable (95%). All of the results from Ontario peaches (100%) were non-detectable.

4.1.4 Vegetables

Very low levels (1 to 3 ppt) of O_8CDD were found in all potato samples. No other PCDD or PCDF residues

TABLE 4.3 : RESIDUES OF PCDD AND PCDF IN POTATOES AND APPLE SAMPLES*

	POTATOES			APPLES		
	Ontario**	P.E.I.**	U.S.A.**	Ontario	New York**	B.C.**
T_4CDD	ND(2)	ND(0.1)	ND(0.6)	ND(0.8)	ND(1)	ND(2)
P_5CDD	ND(1)	ND(0.1)	ND(0.2)	ND(0.6)	ND(1)	ND(0.5)
H_6CDD	ND(0.3)	ND(0.1)	ND(0.1)	ND(0.7)	ND(0.6)	ND(0.4)
H_7CDD	ND(0.2)	ND(0.1)	ND(0.4)	ND(0.4)	ND(0.4)	ND(0.3)
O_8CDD	1	3	3	ND(2)	8	ND(2)
Total:	1	3	3	ND	8	ND
T_4CDF	ND(2)	ND(2)	ND(0.1)	ND(2)	ND(10)	ND(1)
P_5CDF	ND(1)	ND(0.1)	ND(0.6)	ND(0.7)	ND(1)	ND(0.6)
H_6CDF	ND(0.5)	ND(0.1)	ND(0.1)	ND(0.4)	ND(0.6)	ND(0.5)
H_7CDF	ND(0.2)	ND(0.1)	ND(0.1)	ND(0.5)	ND(0.5)	ND(0.4)
O_8CDF	ND(0.3)	ND(0.1)	ND(0.1)	ND(0.3)	ND(0.4)	ND(0.4)
Total:	ND	ND	ND	ND	ND	ND

* All data in pg/g, parts per trillion, corrected for spike recovery.

** Single determination only, all other data are averages of two replicate determinations

ND: Not detected at detection limit given in brackets (ppt)

NR: Not replicated. Value in brackets was determined in one replicate only.

TABLE 4.4 : RESIDUES OF PCDD AND PCDF IN TOMATO,PEACH AND WHEAT SAMPLES*

	TOMATOES		PEACHES		WHEAT	
	Ontario**	U.S.A.**	Ontario	U.S.A.**	Ontario**	Western Canada**
T_4CDD	ND(0.3)	ND(1)	ND(0.5)	ND(0.5)	ND(0.7)	ND(0.6)
P_5CDD	ND(0.1)	ND(0.3)	ND(0.3)	ND(0.5)	ND(0.7)	ND(0.6)
H_6CDD	ND(0.4)	ND(0.4)	ND(0.2)	ND(0.2)	ND(0.3)	ND(0.3)
H_7CDD	ND(0.2)	ND(0.3)	ND(0.3)	ND(0.1)	ND(0.2)	ND(0.2)
O_8CDD	ND(0.6)	ND(0.8)	ND(2)	0.6(0.3)	0.6 (0.3)	0.7 (0.3)
Total:	ND	ND	ND	0.6	0.6	0.7
T_4CDF	ND(3)	ND(1)	ND(1)	ND(3)	ND(4)	ND(5)
P_5CDF	ND(2)	ND(0.4)	ND(0.3)	ND(0.5)	ND(0.7)	ND(0.6)
H_6CDF	ND(0.2)	ND(0.4)	ND(0.2)	ND(0.2)	ND(0.3)	ND(0.8)
H_7CDF	ND(0.3)	ND(0.3)	ND(0.3)	ND(0.1)	ND(0.3)	ND(0.4)
O_8CDF	ND(0.2)	ND(0.4)	ND(0.3)	ND(0.1)	ND(0.3)	ND(0.4)
Total:	ND	ND	ND	ND	ND	ND

* All data in pg/g, parts per trillion, corrected for spike recovery.

** Single determination only, all other data are averages of two replicate determinations

ND: Not detected at detection limit given in brackets (ppt)

NR: Not replicated. Value in brackets was determined in one replicate only.

were found at sub-ppt levels of detection (Table 4.3).

Out of the 30 analytical determinations of the 10 isomer groups reported for potatoes, 27 were non-detectable (90%).

No residues were found in tomatoes at similar low levels of detection (Table 4.4).

4.1.5 Wheat

Sub-ppt levels of O_8CDD were found in both Ontario and Western Canada wheat samples. No other PCDD or PCDF were found at extremely low levels of detection (Table 4.4).

Eighteen out of 20 analytical determinations of the 10 isomer groups were non-detectable (90%).

4.1.6 Summary

These results indicate that the fruit and vegetables samples analysed are substantially free of most PCDD and PCDF, especially the more toxic tetra-, penta- and hexachlorinated forms.

This is a significant finding as the samples were not peeled. The skins of fruit and vegetables would be anticipated to contain PCDD and PCDF if there was uptake due to exposure to PCDD and PCDF from airborne particulates or soil.

Generally, very low levels of O_8CDD were found in egg, chicken, beef, hamburger, potato, apple, peaches and wheat samples. The Quebec chicken and U.S. egg samples contained higher PCDD and PCDF residues, ranging from 5 to 15 ppt, with one result of 210 ppt OCDD.

While all detectable residue results were very low, Ontario plant and animal products had consistently lower PCDD and PCDF residues than samples from other geographical areas within or outside Canada.

Overall, the residue levels found in this study are substantially less than those found in the Davies and Macpherson (1986) report (Table 5.1). Other recently published Canadian, German and U.S. food monitoring studies (Firestone, et al., 1986; Ryan, et al., 1985a; Mathar et al., 1987) and Appendix B also indicate that PCDD and PCDF residues are generally non-detectable, similar to the results from the present study, except in special cases of known pentachlorophenol contamination.

4.2 Organochlorine Pesticides and Industrial Chemicals

The results of analyses of 25 of the 26 food composite samples appear in Tables 4.5, 4.6, 4.7 and 4.8 along with detection limits given in ng/g (ppb). The strawberry data are not reported due to improper storage of samples (See Appendix A.2.1.2(x). The Maximum Residue Limits (MRLs) appear in Table 4.9 and are given in ug/g (ppm) (Food and Drugs Act and Regulations, 1986). The highest results are summarized in Table 4.10 for comparison of MRL with detection limit and residue levels found in fruit, vegetables, grain, meat and egg samples. No residues exceeded the MRLs and indeed, the detected residues were 10 to 500 times lower.

Analysis of the composite samples indicated several contaminant (pesticide and industrial chemicals) residues were detected. The concentrations were low (0.00026 to 0.001 ug/g). In the case of industrial chemical contaminants, no residues of PCB or mirex were detected. HCB residues when detected (B.C. apples, Ontario hamburgers, U.S. prime beef and N.Z. processed beef) were below 1 ng/g. Pentachlorophenol residues were found in most food samples with values ranging from 0.2 to 4.8 ng/g.

Overall, the samples contained residues at concentrations that are frequently observed in other OMAF, Canadian and U.S. monitoring studies (see Section 1.1.3).

TABLE 4.5 : RESIDUES OF ORGANOCHLORINE PESTICIDES AND INDUSTRIAL CHEMICALS IN FRUIT VEGETABLES AND GRAIN SAMPLES (1)

	CONTENT IN SAMPLE AS RECEIVED (ng/g)											
	HCH		Hepta-	Heptachlor		Chlordane			Endosulfan			Dicofol
SAMPLE DESCRIPTION	beta	gamma	chlor	epoxide	Aldrin	alpha	gamma	oxy	I	II	sulfate	
Ontario apples	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	23
B.C. apples	ND	ND	ND	ND	ND	ND	ND	ND	ND	3.9	7.1	ND
N.Y. State apples	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ontario peaches	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	27
U.S. peaches	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ontario tomatoes	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
U.S. tomatoes	ND	ND	ND	ND	ND	ND	ND	ND	1.0	ND	2.1	ND
Ontario potatoes	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PEI potatoes	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
U.S. potatoes	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ontario wheat	ND	0.45	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Western Canada wheat	ND	0.76	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Detection limit	<.02	<0.2	<0.5	<0.2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<1	2

TABLE 4.6 : RESIDUES OF ORGANOCHLORINE PESTICIDES AND INDUSTRIAL CHEMICALS IN FRUIT, VEGETABLE AND GRAIN SAMPLES (2)

	CONTENT IN SAMPLE AS RECEIVED (ng/g)												
SAMPLE DESCRIPTION	DDE	TDE	o,p'-DDT	p,p' DDT	Dieldrin	Endrin	Methoxy-chlor	Mirex	PCB	HCB	T_3CP	T_4CP	P_5CP
Ontario apples	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.71
B.C. apples	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.26	ND	0.24	0.70
N.Y. State apples	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	4.8
Ontario peaches	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.63
U.S. peaches	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.54
Ontario tomatoes	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.13	0.44
U.S. tomatoes	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.05	0.55
Ontario potatoes	ND	ND	ND	ND	1.2	ND	ND	ND	ND	ND	ND	ND	0.36
PEI potatoes	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.40
U.S. potatoes	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.48
Ontario wheat	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.22
Western Canada wheat	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	4.8
Detection limit	<0.5	<1	<1	<1	<0.5	<1	<2	<1	<0.2	<0.2	<0.05	<0.05	<0.05

TABLE 4.7 : RESIDUES OF ORGANOCHLORINE PESTICIDES AND INDUSTRIAL CHEMICALS IN MEAT AND EGG SAMPLES (1)

	CONTENT IN SAMPLE AS RECEIVED (ng/g)										
	HCH		Hepta-	Heptachlor		Chlordane			Endosulfan		
SAMPLE DESCRIPTION	beta	gamma	chlor	epoxide	Aldrin	alpha	gamma	oxy	I	II	sulfate
West Ontario eggs	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
East Ontario eggs	ND	ND	ND	0.47	ND	ND	ND	ND	ND	ND	ND
U.S. eggs	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ontario hamburger	ND	0.42	ND	0.86	ND	ND	ND	ND	ND	ND	ND
New Zealand hamburger	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
East Ontario pork	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
West Ontario pork	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Quebec pork	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ontario chickens	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Quebec chickens	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
U.S. chickens	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ontario prime beef	ND	ND	ND	0.35	ND	ND	ND	ND	ND	ND	ND
U.S. prime beef	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Detection limit	<0.2	<0.2	<0.5	<0.2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<1

TABLE 4.8 : RESIDUES OF ORGANOCHLORINE PESTICIDES AND INDUSTRIAL CHEMICALS IN MEAT AND EGG SAMPLES (2)

	CONTENT IN SAMPLE AS RECEIVED (ng/g)												
SAMPLE DESCRIPTION	DDE	TDE	o,p'-DDT	p,p'-DDT	Dieldrin	Endrin	Methoxy-chlor	Mirex	PCB	HCB	T_3CP	T_4CP	P_5CP
West Ontario eggs	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.80
East Ontario eggs	1.2	ND	ND	ND	1.5	ND	ND	ND	ND	ND	ND	ND	ND
U.S. eggs	0.62	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.95
Ontario hamburger	7.2	ND	ND	ND	3.2	ND	ND	ND	ND	0.57	ND	ND	0.47
New Zealand hamburger	1.7	ND	ND	ND	ND	ND	ND	ND	ND	0.20	ND	ND	3.1
East Ontario pork	1.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.42	0.98
West Ontario pork	4.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.69	2.70
Quebec pork	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.4
Ontario chickens	0.59	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	4.9
Quebec chickens	0.61	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.1
U.S. chickens	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.0
Ontario prime beef	0.95	ND	ND	ND	0.55	ND	ND	ND	ND	ND	ND	ND	3.2
U.S. prime beef	1.6	ND	ND	ND	ND	ND	ND	ND	ND	0.21	ND	ND	2.8
Detection limit	<0.5	<1	<1	<1	<0.5	<1	<2	<1	<5	<0.2	<0.05	<0.05	<0.05

TABLE 4.9 : MAXIMUM RESIDUE LIMITS (MRL) FOR ORGANOCHLORINE PESTICIDES AS SPECIFIED IN THE FOOD AND DRUGS ACT AND REGULATIONS (1986)

COMMON OR (TRADE NAME)	MAXIMUM RESIDUE LIMIT PPM	FOODS
Aldrin and dieldrin	0.2[1]	Meat, meat by-products and fat of cattle, goats, hogs, poultry and sheep.
	0.1[1]	Butter, cheese, milk and other dairy products.
Chlordane (including alpha, gamma and oxy chlordane)	0.1	Butter, cheese, milk and other dairy products; meat and meat by-products of cattle, goats, hogs, poultry and sheep.
DDT	5.0	Fish.
(including the metabolites DDE, TDE, and DDD)	1.0 [1]	Butter, cheese, milk and other dairy products; meat, meat by-products and fat of cattle, hogs, poultry and sheep.
	0.5	Eggs, fresh vegetables.
Dicofol	5.0	Citrus fruits
	3.0	Almonds, apples, apricots, beans, blackberries, boysenberries, cantaloupes, cherries, chestnuts, cucumbers, dewberries, eggplants, figs, filberts, grapes, hickory nuts, honeydew melons, loganberries, muskmelons, peaches, pears, peas, pecans, peppers, pimentos, plums, pumpkins, quinces, raspberries, soybeans, strawberries, summer squash, tomatoes, walnuts, watermelons, winter squash.
	0.1[1]	Butter, cheese, milk and other dairy products, meat and meat by-products of cattle, goats, hogs, poultry and sheep.

TABLE 4.9 - continued

COMMON OR (TRADE NAME)	MAXIMUM RESIDUE LIMIT PPM	FOODS
Endosulfan	2.0	Apples, apricots, broccoli, Brussel sprouts, cabbage, cherries, lettuce, peaches, pears, plums, spinach.
(I, II and the sulfate metabolite)	1.0	Artichokes, beans, cauliflower, celery, cucumbers, eggplants, grapes, melons, peppers, pumpkins, squash, strawberries, tomatoes, watercress.
	0.5	Peas.
	0.1[1]	Butter, cheese, milk and other dairy products; meat and meat by-products of cattle, goats, hogs, poultry and sheep.
Endrin	0.02[1]	Butter, cheese, milk and other dairy products.
Alpha-HCH (BHC isomers except lindane)	0.1[1]	Butter, cheese, milk and other dairy products; meat and meat by-products of cattle, goats, hogs, poultry and sheep.
Gamma-HCH (lindane) ≠	3.0	Apples, apricots, asparagus, avocados, broccoli, Brussels sprouts, cabbage, cauliflower, celery, cherries, collards, cucumbers, eggplants, grapes, guavas, kale, kohlrabi, lettuce, mangoes, melons, mushrooms, mustard greens, okra, onions, peaches, pears, peppers, pineapple, plums, pumpkins, quinces, spinach, squashes, strawberries, Swiss chard, tomatoes.
	2.0[1]	Meat, meat by-products and fat of cattle, goats, hogs and sheep.

TABLE 4.9 - continued

COMMON OR (TRADE NAME)	MAXIMUM RESIDUE LIMIT PPM	FOODS
	0.7 [1]	Meat and meat by-products of poultry.
	0.2 [1]	Butter, cheese, milk and other dairy products.
Heptachlor and its epoxide	0.2 [1]	Meat, meat by-products and fat of cattle, goats, hogs, poultry and sheep.
	0.1 [1]	Butter, cheese, milk and other dairy products
Methoxychlor	14.0	Apples, apricots, asparagus, beans, beets, blackberries, black-eyed peas, blueberries, broccoli, Brussels sprouts, cabbage, carrots, cauliflower, cherries, collards, corn (in the husk), cranberries, cucumbers, currants, eggplants, gooseberries, grapes, kale, kohirabi, lettuce, loganberries, melons, mushrooms, peaches, peanuts, pears, peas, peppers, pineapple, plums, pumpkins, quinces, radishes, raspberries, spinach, squash, strawberries, summer squash, tomatoes, turnips (rutabagas).
	3.0 [1]	Meat, meat by-products and fat of cattle, hogs and sheep.
	2.0	Barley, corn (as grain), oats, rice, rye, soybean, wheat.

[1] calculated on the fat content

TABLE 4.10 : MAXIMUM CONCENTRATIONS OF SELECTED PERSISTENT TOXIC ORGANOCHLORINES DETECTED IN ONTARIO MINISTRY OF THE ENVIRONMENT/ONTARIO MINISTRY OF AGRICULTURE AND FOOD JOINT FOOD STUDY, 1988. FOOD GROUPS REPRESENT ONTARIO, CANADA AND U.S. SOURCES (Results in ug/g, parts per million)

CHEMICAL	MRL*	MINIMUM DETECTION LIMIT	TOMATOES	FRUIT	POTATOES	EGGS/MEAT	WHEAT
alpha-HCH	0.1	0.0002	ND	ND	ND	ND	ND
Lindane	0.2-3	0.0002	ND	ND	ND	0.00042	0.00076
Heptachlor)	0.1-0.2	0.0005	ND	ND	ND	ND	ND
Heptachlor epoxide)		0.0002	ND	ND	ND	0.00086	ND
Aldrin	0.1-0.2	0.0005	ND	ND	ND	ND	ND
alpha-chlordane)		0.0005	ND	ND	ND	ND	ND
gamma-chlordane)	0.1	0.0005	ND	ND	ND	ND	ND
Oxychlordane)		0.0005	ND	ND	ND	ND	ND
Endosulfan-I)		0.0005	0.001	ND	ND	ND	ND
Endosulfan-II)	0.1-2	0.0005	ND	0.0039	ND	ND	ND
Endosulfan sulphate)		0.001	ND	0.0071	ND	ND	ND
Dicofol	0.1-5	0.002	ND	0.027	ND	NA	ND
DDE)		0.0005	ND	ND	ND	0.0072	ND
TDE)	0.5-1	0.001	ND	ND	ND	ND	ND
p,p'-DDT)		0.001	ND	ND	ND	ND	ND
DDT)		0.001	ND	ND	ND	ND	ND
Dieldrin	0.1-0.2	0.0005	ND	ND	0.0012	0.0032	ND
Endrin	0.02	0.001	ND	ND	ND	ND	ND
Methoxychlor	2-14	0.002	ND	ND	ND	ND	ND
PCB	-	0.0002	ND	ND	ND	ND	ND
Mirex	-	0.001	ND	ND	ND	ND	ND
Hexachlorobenzene	-	0.0002	ND	0.00026	ND	0.00057	ND
2,4,5-trichlorophenol	-	0.00005	ND	ND	ND	ND	ND
2,3,4,6-tetrachlorophenol	-	0.00005	ND	0.00024	ND	0.00069	ND
Pentachlorophenol	-	0.00005	0.0005	0.0048	0.0014	0.0049	0.0048

ND = not detected; NA = not analysed

* MRL may not apply to all commodities listed (see Table 4.9)

5.0 DISCUSSION AND CONCLUSIONS

5.1 PCDD and PCDF Residues in Food

5.1.1 Comparison of PCDD and PCDF Results with Other Current Studies

There are a number of marked differences between the results of the present study and the earlier values reported by Davies and Macpherson (1986). For example, they reported high values of several thousand ppt of H_7CDD, H_7CDF and O_8CDF in the fruit-sample (Table 5.1). In the present study residues in fruit samples were largely non-detectable or in the sub-ppt to low ppt range. In separate studies, HWC and the federal German government were unable to detect PCDD or PCDF in fruit samples at sub-ppt levels of detection (minimum detection limits of 0.5 ppt and 0.02 ppt, respectively) (Appendix B, Mathar et al., 1987).

Theoretical calculations also suggest that PCDD and PCDF are unlikely to be absorbed by vegetation (Travis and Arms, 1988).

Since the levels found in fruit in the Davies and Macpherson report exceed levels reported for Ontario urban soils (MacLaughlin et al., 1987) this sample may have been contaminated subsequent to sampling. Certainly, unpublished results of a subsequent fruit sample analysed as part of the Davies and Macpherson study showed no detectable levels of most PCDD or PCDF (K. Davies, personal communication).

The Davies and Macpherson (1986) study does not report what analytical QA/QC was employed, so it is not possible to evaluate its reliability. In 1986, MOE staff attempted to perform further analyses of the food extracts prepared in the Davies and Macpherson study. Unfortunately, neither aliquots of the extracts or non-extracted homogenates nor the original GC/MS printouts from which the results were calculated were retained by the contractor from the

TABLE 5.1 : CONCENTRATIONS OF PCDD AND PCDF IN FOOD COMPOSITES BASED ON TABLE 6 FROM DAVIES AND MACPHERSON (1986) (pg/g, parts per trillion)

CONGENER GROUP	MINIMUM DETECTION LIMIT	ROOT VEG. INCLUDING POTATOES	FRUIT	LEAFY VEGETABLES	MILK	MEAT/EGGS
T_4CDF	0.1	ND	45	ND	120	50
T_4CDD	0.1	ND	ND	0.4	2.5	ND
P_5CDF	1.0	ND	280	ND	7.6	16
P_5CDD	1.0	ND	5	ND	ND	ND
H_6CDF	1.0	2	2000	ND	ND	ND @ 5000*
H_6CDD	1.0	ND	450	ND	ND	ND
H_7CDF	1.0	39	6600	ND	13	ND
H_7CDD	1.0	12	1200	ND	3.4	ND
O_8CDF	1.0	130	1200	ND	58	1.8
O_8CDD	1.0	10	120	ND	36	ND

ND - Not detected

* high background due to interference

Davies and Macpherson study, (personal communication, Zenon Environmental and K. Davies). This precluded any further investigation of the causes for the large discrepancies between the Davies and Macpherson (1986) results and those reported in the current study.

5.1.2 Calculated Dietary Intakes of PCDD and PCDF

Under the Food and Drugs Act and Regulations (1986) foods containing PCDD, other than fish containing less than 20 parts per trillion of 2,3,7,8-TCDD are considered adulterated and not fit for sale. There are no regulations for PCDF in foods.

Currently work is underway by federal/provincial committees to develop national guidelines for PCDD and PCDF in all environmental media. This work is based on a new multi-media approach to regulation of persistent environmental contaminants, which takes into account all routes of human exposure, (air, water, diet, etc.). This approach will ensure that guidelines are set to ensure that the total exposure from all sources of PCDD and PCDF do not exceed the maximum allowable daily intake (MOE/HWC, in preparation). The recommended maximum allowable daily intake for all PCDD and PCDF is the toxic equivalent of 10 pg of 2,3,7,8-TCDD/kg body weight (MOE, 1985a; MOE/HWC, in preparation).

In the interim, an analysis of current estimated exposures from the diet compared with the maximum allowable daily intake is presented to provide an evaluation of health risk.

Estimates of the relative toxicity of other PCDD and PCDF to 2,3,7,8-TCDD were calculated using toxicity equivalence factors (TEF) which facilitate conversion of measured concentrations to an equivalent concentration of 2,3,7,8-TCDD (Table 5.2). Table 5.2 contains an international scheme of

TEF recently developed by Canada, Ontario, U.S.A, the Netherlands and Sweden (Dioxin, 1987 - in press). These international TEF are similar to those developed by MOE (1985a) and result in comparable 2,3,7,8-TCDD equivalent values. The international TEF were used to calculate the toxicity equivalents (TEQ) found in Table 5.3.

PCCD and PCDF food residue data from the present study, the international TEF values and average Canadian consumption factors were used to derive dietary intakes for comparison with the maximum allowable daily intake. Absorption by the gastrointestinal tract was assumed to be 100%. Exposures were based on reported average Canadian adult intakes, therefore, this assessment should not be used to infer health risks for specific individuals whose dietary intake and food product choices are widely different from the Canadian average.

TABLE 5.2 : INTERNATIONAL TOXICITY EQUIVALENCY FACTORS (TEF) FOR CONGENERS OF PCDD AND PCDF*

CONGENER	TEF
2,3,7,8-T_4CDD	1
1,2,3,7,8-P_5CDD	0.5
1,2,3,6,7,8-H_6CDD)	0.1
1,2,3,6,7,8-H_6CDD)	
1,2,3,6,7,8-H_6CDD)	
1,2,3,4,6,7,8-H_7CDD	0.01
OCDD	0.001
2,3,7,8-T_4CDF	0.1
2,3,4,7,8-P_5CDF	0.5
1,2,3,7,8-P_5CDF	0.01
1,2,3,4,7,8-H_6CDF)	0.1
1,2,3,7,8,9-H_6CDF)	
1,2,3,6,7,8-H_6CDF)	
2,3,4,6,7,8-H_6CDF)	
1,2,3,4,6,7,8-H_7CDF)	0.01
1,2,3,4,7,8,9-H_7CDF)	
OCDF	0.001

* Proposed international scheme for TEF (NATO CCMS TEF Subgroup, 1987, Chemosphere, in press)

TABLE 5.3 : CALCULATED DAILY INTAKE OF PCDD AND PCDF VIA RESIDUES IN FOOD FROM CURRENT STUDY

FOOD GROUP	DAILY CONSUMPTION (g/person/day)[1] whole wt	2,3,7,8-TCDD Equivalents[2] (pg TEQ[4]/g whole wt)	DAILY INTAKE pg TEQ/ person[3]	DAILY INTAKE pgTEQ/kg body weight
Beef	55.8	0.29	16.2	0.27
Pork	19	0.03	0.6	0.01
Poultry	20	0.39	7.8	0.13
Eggs	29	0.59	17.0	0.28
Milk Products	444	0.11	48.8	0.81
Fruit	190	0.004	0.76	0.013
Vegetables	220	0.002	0.44	0.007
Wheat Based Products	125	0.0007	0.09	0.001
		Total:	91.7	1.52[5]

[1] - Nutrition Canada, 1977
[2] - Values from Tables 3.1, 4.1, 4.2, 4.3, 4.4, C.1 and C.2
[3] - 60 kg adult
[4] - TEQ = toxic equivalent
[5] - Maximum allowable daily intake for comparison = 10.0 pg 2,3,7,8-TCDD TEQ/kg body weight

The data found in Tables 3.1, 4.1, 4.2, 4.3, 4.4 and Appendix C, Table C.1 and C.2 have been used to calculate the daily intake of PCDD and PCDF from food available in Ontario (Table 5.3). The TEF found in Table 5.2 for the most toxic isomer in each isomer group of PCDD or PCDF has been applied to the whole isomer group. For example, for P_5CDD, the TEF of 0.5 for 1,2,3,7,8-P_5CDD is applied to all of the P_5CDD measured in a sample. This approach may overestimate the actual risk of the mixture.

The daily intake estimate of PCDD and PCDF in TEQ for each food group is calculated from the product of the average TEQ values for each food group multiplied by the daily consumption of that food. The daily consumption of food estimates are from Nutrition Canada (1977). These are the values used by Health & Welfare Canada in setting food residue limits. They are judged to be the most accurate estimates of actual food eaten. Therefore, these estimates of food intake in turn provide the most accurate estimate of exposure to food contaminants.

The Nutrition Canada (1977) food intakes (Table 5.2, Column 2) are based on 24 hour dietary recall values and differ from the food intake estimates used by Davies and Macpherson (1986) which were derived from estimated annual food purchases for a typical Ontario household (Statistics Canada, 1982b.). Statistics Canada (1982b) estimated annual food purchases based on quantities of raw produce purchased in stores and did not take into account wastage of food during storage and preparation prior to consumption.

From the information presented in Table 5.3, several major points are evident:

- The food which contributed the most exposure to PCDD and PCDF was milk, followed by eggs and beef.

- The calculated total daily intake of PCDD and PCDF from food is 1.52 picogram of TEQ per kilogram body weight.

- The total contribution from the animal products to the daily intake is 1.5 picograms TEQ per kilogram body weight (about 99% of the total).

- The plant products contribute 0.02 picograms of TEQ per kilogram body weight per day (about 1% of the total).

- The calculated intake of PCDD and PCDF from the food analyzed in this study is about 15% of the maximum allowable intake from all sources.

Fish were not analysed in the present study. To estimate the added contribution from fresh water fish to dietary intake, a reasonable estimate of 0.27 picogram TEQ per kilogram body weight per day has been made (Ontario Ministry of the Environment and Health & Welfare Canada, in press). This would bring the daily exposure to 1.79 pg TEQ/kg body weight (about 18% of the maximum allowable daily exposure).

To provide a worst case estimate of the possible concentration of PCDD and PCDF in food, intakes were also estimated using positive values for the non-detectable results from this study. This very conservative approach assumes that the contaminant is present at some level near the minimum detection level. Additional analyses were performed at the MOE Laboratory to determine the minimum detection levels for this study. The results of this work are found in Appendix C, Table C.2. Based on this work and data published by the Federal German Food Study (Mathar et al., 1987), detection limits in the sub-ppt range are achievable, e.g. 0.02 ppt. Substituting these minimum detection limit values for the non- detectable results in the present study the worst case estimate of exposure from food intake (including freshwater fish) was 2.28 pg TEQ/kg body weight/day or about 23% of the maximum allowable daily intake.

While the total exposure estimate is increased using this worst case approach, the total exposure is still well below the maximum allowable daily intake. Clearly additional food analysis programs which are targeted at reaching lower detection limits would be useful in establishing the maximum quantities of PCDD and PCDF present in the food supply.

To place the calculated food intake in context, the results of a multi-media exposure assessment showing intakes from other routes of environmental exposure to PCDD and PCDF (adapted from Ontario Ministry of the Environment and Health & Welfare Canada, in press) is shown below.

pg TEQ/kg body weight/day

Air	0.07
Water	0.002
Soil	0.03
Consumer Products	0.01

Based on this assessment and using the worst case assumptions for food intake, total exposure to PCDD and PCDF is 2.39 picogram TEQ/kg body weight/day. This total exposure estimate is about 24% of the maximum allowable daily intake.

Food intake (including freshwater fish) is the largest exposure pathway, accounting for 95% of the exposure, or about 23% of the maximum allowable daily intake.

Details of these calculations are included in a report by Ontario Ministry of the Environment and Health & Welfare Canada, in press.

5.1.3 Conclusions from PCDD and PCDF Results

In conclusion, it can be seen that the conservative estimates of dietary exposure to PCDD and PCDF shown in Table 5.3 and the text indicate that exposure to PCDD and PCDF from consumption of commercially available food in Ontario is well below the maximum allowable daily intake.

5.2 Pesticide Residues in Food

5.2.1 Comparison of Results with Other Current Studies

The residue levels found by Davies and Macpherson (1986) are, in general, of similar magnitude to the observations in this study (Table 4.10) and other OMAF, Canadian and U.S. studies (Gantrell et al., 1985a,b,c,d. 1986a,b,; FRMCP, 1985)

Many of the residues reported by Davies and Macpherson (1986) were below the detection limit of the OMAF Laboratory (Table 5.4). For example, they reported gamma-chlordane residues of ND (< 0.01 ng/g) to 0.06 ng/g whereas OMAF data reported ND (<0.5 ng/g). With several other pesticides, their detection limit was 2 to 100 times lower than the OMAF laboratory, thus indicating trace residues where OMAF detected none. Detection limits in U.S. surveys are similar to those of the OMAF laboratory (Gartrell et al., 1986a,b). The detection limits achieved in the OMAF analysis for specific contaminants are several times lower than the MRL to ensure that the food product is in compliance with food safety regulations (the Food and Drugs Act and Regulation, 1986).

TABLE 5.4 : COMPARISON OF DETECTION LIMITS (ug/g) FOR ORGANOCHLORINE COMPOUNDS IN FOOD

CHEMICAL	MINIMUM DETECTION LIMIT (ug/g)		FACTOR
	Davies Report	OMAF	
alpha-HCH	0.00001	0.0002	20
gamma-HCH (lindane)	0.00001	0.0002	20
heptachlor	0.00001	0.0005	50
heptachlor epoxide	0.00001	0.0002	20
aldrin	0.00001	0.0005	50
alpha-chlordane	0.00001	0.0005	50
gamma-chlordane	0.00001	0.0005	50
oxychlordane	0.00001	0.0005	50
endosulfan-I	0.00001	0.0005	50
endosulfan-II	0.00001	0.0005	50
endosulfan sulphate	NA	0.001	--
DDE	0.00001	0.0005	50
TDE	0.00001	0.001	100
o,p'-DDT	0.00001	0.001	100
p,p'-DDT	0.00001	0.001	100
dieldrin	0.00001	0.0005	50
endrin	0.00001	0.001	100
methoxychlor	0.0001	0.002	20
PCB	0.0001	0.0002	2
mirex	0.00001	0.001	100
hexachlorobenzene	0.00001	0.0002	20

Detection limits for U.S. studies are almost identical to the OMAF levels.

NA - not analysed

A comparison may be made between the Davies and Macpherson (1986) results (Table 5.5) and those in the OME/OMAF study (Tables 4.5 to 4.8). One anomaly of the Davies and Macpherson (1986) data was the distribution of DDT isomers. The high proportion of parent DDT observed in their samples would indicate recent applications of DDT. This is unlike the high proportion of DDE found in surveys conducted by OMAF. DDE, the major metabolite of DDT, is formed after a period of time in the environment. Hence, a high proportion of DDE indicates historic applications of DDT.

U.S. studies indicate that most of the current total DDT residue is DDE; in fact, Gartrell *et al.*, (1985a,b,c,d; 1986a,b) show about a 100:1 DDE:DDT ratio. The results of Davies and Macpherson (1986) data indicate more DDT than DDE in leafy vegetables, root vegetables and milk. Currently there are no approved uses of DDT in food production in North America.

Surveys by OMAF of residues in Ontario milk (see Table 5.6) indicate that DDE residues predominate.

TABLE 5.5 : CONCENTRATIONS OF SELECTED PERSISTENT ORGANOCHLORINE COMPOUNDS FOUND IN VARIOUS FOODSTUFFS, AS REPORTED IN TABLE 5 OF THE DAVIES AND MACPHERSON REPORT (1986)

Table 11 : Concentrations of Selected Persistent Toxic Organochlorines Detected in Food Composites (1985) (ug/g)

	MINIMUM DETECTION LEVEL	LEAFY VEG.	FRUIT	ROOT VEG. INCLUDING POTATOES	MILK	EGGS/MEAT
1,3-Dichlorobenzene	0.0001	ND	0.0044	0.0011	0.0014	ND
1,4-Dichlorobenzene	0.0001	ND	ND	ND	0.0055	ND
1,2-Dichlorobenzene	0.0001	ND	ND	ND	ND	0.0018
1,3,5-Trichlorobenzene	0.00001	0.00028	0.00012	ND	0.00012	0.0007
1,2,4-Trichlorobenzene	0.00001	0.0004	0.00014	ND	0.00014	0.00074
1,2,3-Trichlorobenzene	0.00001	0.00011	ND	ND	ND	ND
1,2,3,5/1,2,4,5-Tetrachlorobenzene	0.00001	ND	ND	ND	ND	N
1,2,3,4-Tetrachlorobenzene	0.00001	ND	ND	ND	ND	ND
Pentachlorobenzene	0.00001	ND	ND	ND	ND	ND
Hexachlorobenzene	0.00001	0.00002	ND	0.00004	0.00016	0.00017
A-HCH	0.00001	ND	0.00002	ND	0.00013	0.00013
G-HCH	0.00001	0.00007	0.0001	0.00005	ND	0.0021
Heptachlor	0.00001	ND	ND	ND	ND	ND
Aldrin	0.00001	ND	ND	ND	ND	ND
Oxychlordane	0.00001	0.00004	ND	ND	0.00008	0.00013
Heptachlor Epoxide	0.00001	ND	ND	ND	0.00021	0.00012
A-Chlordane	0.00001	ND	0.00013	0.0001	0.0001	0.00012
G-Chlordane	0.00001	0.00006	0.00006	0.00004	0.00002	ND
Endosulfan I	0.00001	0.0038	0.0014	ND	ND	ND
p,p'-DDD	0.00001	0.0002	0.0046	0.00039	0.00027	0.0031
Dieldrin	0.00001	0.0031	0.00011	0.023	0.0019	0.0031
Endrin	0.00001	0.00032	0.00027	0.00037	0.00027	ND
Endosulfan II	0.00001	0.017	0.0057	0.00071	0.0022	ND
p,p'-TDE	0.00001	0.00034	ND	0.00047	ND	0.00017
o,p'-DDT	0.00001	0.00002	ND	ND	ND	ND
p,p'-DDT	0.00001	0.00042	0.00039	0.065	0.0014	0.00031
Photomirex	0.00001	ND	ND	ND	ND	ND
Mirex	0.00001	ND	ND	ND	ND	ND
Methoxychlor	0.0001	ND	ND	ND	ND	ND
Total PCB	0.0001	ND	0.0007	ND	0.0001	0.0003

Note: ND = not detected
B = beta
A = alpha
G = gamma

TABLE 5.6 : PROPORTION OF DDE IN ONTARIO MILK

YEAR	DDE/Total DDT (%)
1967 - 69	52
1970 - 71	65
1973	83
1977	80
1983	77

5.2.2 Conclusions

No residues of pesticides exceeded the maximum residue limits (MRL) as outlined in the Food and Drugs Act and Regulations (1986). In fact, the detected residues were one tenth to five hundredths of the MRL.

5.3 Organchlorine Contaminant Residues in Food

As pointed out in Section 1.1.3, a distinction is made between residues in food arising from the use of currently registered pesticides in food production and residues arising from past uses of persistent pesticides no longer registered for agricultural use, or non-agricultural pesticides or persistent industrial pollutants. This distinction can be further elaborated into the difference between "avoidable" and "unavoidable" contaminants of food. Unavoidable contaminants occur when, in spite of good agricultural or food manufacturing practices, the presence of the contaminant in food cannot be completely prevented. Such is the case when persistent industrial chemicals or pesticides persist in the environment and cause indirect "unavoidable" contamination of food.

Health and Welfare Canada has established MRL for 19 of the 25 organochlorine pesticide or contaminant residues measured in this study (Table 4.9) of the remaining six pesticides or contaminants analysed for which MRL are not available, detectable residues were reported for hexachlorobenzene, 2,3,4,6-tetrachlorophenol and pentachlorophenol. To provide some estimate of the possible health significance of the presence of these residues in Ontario food, current estimated daily intakes were compared with U.S. and international acceptable daily intakes (ADI) or acceptable risk levels based on low dose carcinogenic risk estimates using the U.S. EPA linear multistage mathematical extrapolation method (this method uses cancer data from animal studies and provides a very conservative estimate of cancer risk).

5.3.1 Hexachlorobenzene

This contaminant, originally used as a fungicide and seed dressing, has been shown to be carcinogenic in laboratory rodents. The U.S. EPA risk estimation method has been adopted by the World Health Organization for development of a drinking water guideline for hexachlorobenzene (WHO, 1984a,b).

The WHO uses an acceptable risk level of less than 1 additional case of cancer per 100,000 population following lifetime daily exposure to carcinogenic substances (this may be expressed as a lifetime cancer risk of 10^{-5}) (WHO, 1984a).

The U.S. generally considers individual lifetime cancer risks of 10^{-6} resulting from lifetime exposure to environmental contaminants to be insignificant.

Maximum daily dietary intakes of hexachlorobenzene may be conservatively estimated using the maximum residue levels for major food groups found in this study (Table 4.10) and the Nutrition Canada food consumption factors (Table 5.3). The maximum daily intake of hexachlorobenzene from fruit, meat and eggs is calculated to be 0.002 ug per kilogram body weight or 0.12 ug per 60 kg person per day. Using the U.S. EPA unit cancer risk factor for hexachlorobenzene of 1.67 $(mg/kg\ body/day)^{-1}$ (EPA, 1985) the calculated lifetime cancer risk of consuming 0.12 ug hexachlorobenzene per 60 kg adult per day is 3.3×10^{-6}.

5.3.2 Pentachlorophenol and 2,3,4,6-tetrachlorophenol

These chemicals are non-agricultural pesticides primarily used in the wood preservation and wood protection industries. Pentachlorophenol is the most toxic member of the chlorophenols. The U.S. NRC (1977) has calculated an ADI of 3 ug/kg body weight per day for pentachlorophenol. This ADI was adopted by WHO for development of drinking water guidelines (WHO, 1984a,b).

A worst case estimate of the maximum daily dietary intake of pentachlorophenol may be made using the maximum residue levels (Table 4.10) and the Nutrition Canada food consumption factors (Table 5.3). The calculated maximum daily intake of pentachlorophenol from fruit, potatoes, wheat, meat and eggs is 0.04 ug per kg body weight or 2.43 ug per 60 kg person per day. This is over 70 times less than the ADI for pentachloro- phenol cited above.

There is no ADI for 2,3,4,6-tetrachlorophenol. This compound is less toxic than pentachlorophenol and levels encountered in this study were over ten times lower than pentachlorophenol.

5.3.3 Conclusions

Of six non-agricultural pesticides and industrial chemical contaminants analysed for, three were not detected. Detectable residues of hexachlorobenzene, 2,3,4,6-tetrachlorophenol and pentachlorophenol do not appear to be significant in terms of public health risk.

5.4 General Conclusions

The general conclusions are outlined below:

- Fruit and vegetable samples were substantially free of PCDD and PCDF residues, especially the more toxic tetra, penta and hexachlorinated forms. Animal products contained residues of PCDD and PCDF since these contaminants are lipophilic.

- Ontario grown plant and animal products had lower or comparable PCDD and PCDF residues than samples imported from other provinces or the U.S.A.

- Overall the residue levels of PCDD and PCDF found in the present study are consistent with recent Canadian, German and U.S. data and are significantly lower than values reported by Davies and MacPherson (1986).

- Based on the present study, the calculated daily intake of PCDD and PCDF from consumption of commercially available food in Ontario is 1.52 picogram of toxic equivalents (TEQ) per kg body weight per day, or 15% of the maximum allowable daily intake of 10 pg TEQ per kg body weight per day proposed by Ontario (MOE, 1985a). Animal products contribute 1.5 picograms TEQ per kg body weight per day or 99%, whereas plant products contribute 0.02 picograms of TEQ per kg body weight per day, or 1% of the total exposure.

- Compared to exposure estimates for other sources (air, water, soil, consumer products) food intake is the largest exposure pathway for the human receptor, accounting for 95% of the total intake of PCDD and PCDF.

- To provide a worse case estimate of intake via the food basket, exposure can also be calculated by assuming that PCDD and PCDF residues are present at the minimum detection levels reported in this study and elsewhere. Using these very conservative assumptions, total exposure via the food pathway is estimated at 2.28 pg of TEQ per kg body weight per day, or 23% of the maximum allowable daily intake.

- No residues of pesticides exceeded the maximum residue limits (MRL) as outlined in the Food and Drugs Act and Regulations (1986). In fact, the detected residues were one tenth to five hundredths of the Maximum Residue Limits (MRL).

- In the case of non-agricultural pesticides and industrial chemical contaminants, no residues of PCB, 2,4,5-trichlorophenol, or mirex were detected. Detectable residues of HCB, 2,3,4,6-tetrachlorophenol and pentachlorophenol were not considered significant in terms of risk to public health.

- Pentachlorophenol, a wood preservative, was found in all food samples, except Eastern Ontario eggs. The presence of low levels of H_6CDD, H_7CDD and O_8CDD in some foods may be related to the P_5CP residues.

- Residues levels of pesticide and other industrial contaminants reported in the present study are consistent with the findings of other OMAF, Canadian and U.S. monitoring studies and confirm the observed trend for declining residues of these compounds in food commodities.

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APPENDIX A
SAMPLE SELECTION COLLECTION AND ANALYTICAL PROCEDURES

As described in Section 2.1 food commodities were selected following analysis of Ontario and Canadian food consumption statistics (Table A.1, A.2 and A.3).

A.1 SAMPLE COLLECTION

As described in Tables 2.1 and 2.2 a total of twelve commodities that ranked as major or primary raw food items for the Ontario consuming public were selected for analysis. Samples were purchased by OMAF. Six animal and six plant products were included. The animal products included raw milk that had been sampled and analysed just prior to commencement of the main study.

A.1.1 Animal Products

Beef:

The following samples were collected by members of the Livestock Inspection Branch:

i) Imported United States prime beef originating from suppliers in Texas and Kansas was sampled and composited from an importer in Guelph, Ontario. The sample consisted of 10 T-bone steaks and was collected on August 19, 1986.

ii) Ontario prime beef was collected from six beef producers in southwestern Ontario and five from eastern Ontario. The farms in the southwest were located in the counties of Bruce, Huron, Lambton, and Middlesex. The farms in eastern Ontario were located in the municipalities of Ottawa-Carleton and Stormont, Dundas and Glengarry. Each of the eleven producers supplied one T-bone steak on August 18, 1986. These were composited to give a single sample for analysis.

A.1: AVERAGE FOOD CONSUMPTION PER HOUSEHOLD IN CANADA BASED ON A SURVEY CONDUCTED FOR THE FOOD INDUSTRY[1]

FOOD COMMODITY	kg/WEEK/ HOUSEHOLD		DIET (%)	
Dairy Products	12.71		28.62	
Cereals	6.12		13.79	
wheat		4.60		10.36
Root crops	4.89		11.00	
potatoes		2.41		5.43
Red Meat	4.80		10.81	
beef		3.19		7.28
Fruit and vegetables	3.18		7.14	
tomatoes		1.28		2.87
cucumbers		1.26		2.84
sweet corn		0.64		1.63
Poultry	2.54		5.71	
eggs		1.23		2.77
chicken		1.14		2.58
Citrus fruit	1.69		3.81	
Seed and pod vegetables	1.63		3.66	
beans		0.81		2.04
Sugar	1.61		3.64	
Pork	1.53		3.43	
Pome fruit	1.24		2.79	
apples		1.13		2.53
Leafy vegetables	1.22		2.76	
Stone fruit	0.55		1.25	
peaches		0.40		0.90
Small fruit	0.37		0.83	
strawberries		0.08		0.18
TOTAL:			99.24	

[1] Food Processors Survey - unpublished

A.2: CANADIAN TOTAL DIET STATISTICS (from Smith, 1971)

	FOOD COMMODITY	CONSUMPTION g/PERSON/DAY		DIET (%)	
I	Milk and Dairy Products	495		27.7	
	(a) Milk		411		23.1
II	Meat; fish, poultry	276		15.5	
	(a) Beef		92.8		5.2
	(i) steak		22.7		1.3
	(ii) hamburger		29.7		1.7
	(b) Pork		59.2		3.3
	(c) Poultry		36.5		2.0
	(d) Eggs		38.2		2.1
III	Cereals	190		10.7	
	(a) Wheat		159		9.0
IV	Root vegetables	241		13.5	
	(a) Potatoes		191		10.7
V	Leafy vegetables	46		2.6	
VI	Legumes	32		1.8	
VII	Fruit-vegetables	82		4.5	
	(a) Tomatoes		75		4.1
VIII	Fruit	193		10.7	
	(a) Apples		48		2.7
	(b) Peaches		11		0.6
IX	Oils and fats	27		1.5	
X	Sugars; adjuncts	142		8.0	
XI	Beverages	59		3.3	
	TOTAL	1784		99.8%	

A.3: ESTIMATE OF PER CAPITA CONSUMPTION IN ONTARIO BASED ON DOMESTIC PRODUCTS AND THE IMPORT/EXPORT TRADE[1]

FOOD COMMODITY	ESTIMATED ONTARIO PER CAPITA CONSUMPTION (kg/yr)	CONSUMPTION IN ONTARIO (tonnes)[2]	ONTARIO PRODUCTION (tonnes)[3]	ONTARIO EXPORT [4] (tonnes)	ONTARIO TOTAL IMPORTS[4] (tonnes)	IMPORTS FROM U.S.A.[4] (tonnes)
Milk	110 L	2,339,000	2,339,000 (KL)			-
Wheat	79.1	717,166	827,800	495,500	374,864	-
Potatoes	38.5	348,600	311,000	11,400	49,000	49,000
Beef	37.2	337,100	318,800	27,100	45,400	22,600
Pork	39.0	308,300	380,300	79,100	7,100	5,900
Tomatoes	28.0	253,854	592,300	2,300	51,100	46,400
Apples	25.9	217,588	144,200	17,800	108,300	37,700
Chicken	26.1	236,600	210,000	900	27,500	27,500
Eggs	15.2	137,400	139,700	5,100	3,300	3,300
Peaches	4.1	27,199	20,600	-	16,400	11,900

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[1] - Based on population of 9,066,200

[2] - Statistics Canada. (1982a)

[3] - OMAF (1985)

[4] - Statistics Canada - External Trade Division

Hamburger:

The following samples were collected by the Livestock Inspection Branch.

i) Imported New Zealand boneless beef was sampled from a source in Kitchener, Ontario. The sample consisted of 5 kg of meat pieces which were obtained on August 19, 1986.

ii) Ontario beef made into hamburger was obtained from a meat packer in the Niagara Peninsula on June 13, 1986. A five-kilogram amount was obtained representing several domestic farm producers from Ontario.

Pork:

The following samples were collected by the Livestock Inspection Branch.

i) West central Ontario-produced pork chops were obtained from 10 farm producers located in the counties of Brant, Durham, Oxford, and Perth. Each farm supplied one pork chop on June 12 or 13, 1986 and these were combined for analysis.

ii) Eastern Ontario-produced pork chops were obtained from 10 farm producers in the municipalities of Ottawa-Carleton, Prescott and Russell, and Stormont, Dundas and Glengarry. Each farm supplied a pork chop on August 18, 1986 and these were combined for analysis.

iii) Pork chops from a carcass bearing a Quebec plant legend were collected from a Toronto area plant.

Chicken-Broilers:

The following samples were collected by the Livestock Inspection Branch.

i) Ontario-produced chicken was obtained from 20 producers across the west central regions of the Province. Each of the 20 producers supplied a whole eviscerated chicken on June 13 or 16, 1986 and these were combined for analysis.

ii) Quebec-produced chicken was collected from a slaughter plant in the Toronto area. The sample included 10 whole chickens.

iii) United States-produced chicken was obtained from chicken imported live for slaughter. Ten whole chickens were combined for the sample.

Hen Eggs:

The following samples were collected by the Livestock Inspection Branch.

i) Eggs produced in western Ontario were obtained from two large farm suppliers located in the county of Middlesex. Each supplied 12 eggs coming from a wide selection of birds. Eggs were collected on August 18, 1986.

ii) Eggs produced in eastern Ontario were supplied by four large farms located in the municipalities of Ottawa-Carleton, Prescott and Russell, and Stormont, Dundas and Glengarry. Each of the four farms supplied six eggs on August 18, 1986.

iii) Eggs produced in the United States came from a large supplier located in Indiana. Twenty-four eggs were picked up from an importer located in the county of Waterloo on August 20, 1986.

Cow's Milk:

The following samples were collected by the Dairy Inspection Branch.

i) Western Ontario milk was obtained from ten farms located in the county of Perth. Each supplied 20 mL from a farm bulk tank which contained two days milk.

ii) Central Ontario milk was collected from 10 farms located in the county of Northumberland. Each supplied 21 mL from a farm bulk tank as described above.

iii) Eastern Ontario milk was collected from 10 farms located in the county of Dundas. Each supplied 21 mL of milk as described above.

iv) Northern Ontario milk was collected from 11 farms located in the districts of Algoma, Manitoulin, Sudbury. Each supplied 21 mL in the same way as described above.

A.1.2 Plant Products

Apples:

Samples were collected by the Fruit and Vegetable Inspection Branch.

i) Ontario-produced apples were obtained from the Ontario Food Terminal wholesale farmers market between August 10 and 20, 1986. The sample (4.5 kg) was made up of early cultivars (Vista Bella, Melba, Wellington, Duchess, Jerseymac) from 10 Ontario apple growers located in the west-central region, (Peel, Niagara, Hamilton-Wentworth).

ii) New York-produced apples were obtained from five Ontario wholesalers and retail stores in the Toronto area. The samples consisted of 4.5 kg apples of cultivars Mutsu, Jonagold, and Golden Delicious.

iii) Pacific coast apples were obtained from the Ontario Food Terminal between August 10 and 20, 1986. The sample was made up of apples from five shippers located in Washington State and two shippers located in British Columbia. The sample contained 4.5 kg (Red and Golden Delicious).

Peaches:

Samples were collected by the Fruit and Vegetable Inspection Branch

i) Ontario-produced peaches were obtained from the Ontario Food Terminal wholesale farmers market between August 10 and 20, 1986. Peaches were collected from 12 growers located in the Niagara Peninsula. The sample was made up of various cultivars totalling 4.5 kg.

ii) United States-produced peaches were obtained from ten Toronto wholesalers. The produce came from growers located in California, New Jersey and North Carolina. The number of cultivars was unknown and the total sample was 4.5 kg.

Potatoes:

Samples were collected by the Fruit and Vegetable Inspection Branch.

i) Ontario-produced potatoes were obtained from the Ontario Food Terminal wholesale farmers market between August 10 and 20, 1986. Three cultivars (Superior, Chieftan and Cherokee) came from eight central Ontario producers and packers.

ii) United States potatoes were obtained at the Ontario Food Terminal from wholesalers. The produce came from growers located in Texas and New Mexico.

Strawberries:

Samples were collected by the Fruit and Vegetable Inspection Branch

i) United States strawberries were collected at the Ontario Food Terminal wholesale market from four suppliers between August 10 and 20, 1986. The sample (5 kg) was not identified for cultivars and came from several shippers all located in California.

ii) Ontario-grown strawberries were collected at the Ontario Food Terminal from nine growers at the wholesale farmers market in early July, 1986.

Tomatoes:

Samples were collected by the Fruit and Vegetable Inspection Branch.

i) Ontario-produced tomatoes were collected at the Ontario Food Terminal between August 10 and 20, 1986. The fruit came from eleven western Ontario producers located in Essex and Haldimand-Norfolk. The samples included six cultivars (Red Pack, Pick Red, Stores Pack, Pick Red 1350, Fresh Pack and TH 318).

ii) United States tomatoes were obtained from five wholesalers at the Ontario Food Terminal between August 10 and 20, 1986. The tomatoes came from shippers located in Virginia, California and Ohio.

Wheat:

Samples were collected by Fruit and Vegetable Inspection Branch.

i) Ontario soft white wheat was collected from two flour mills and one elevator in Toronto on August 15, 1986. Each supplied a 2 L sample, which were composited to form the Ontario wheat sample.

ii) Western Canada hard red wheat was collected from two Ontario flour mills and one elevator in Toronto on August 15, 1986. Each supplied a 2 L sample which were composited to form the Western Canada sample.

A.2 ANALYTICAL PROCEDURES

A.2.1 Sample Preparation and Storage

All sampling was performed by staff of the Ontario Ministry of Agriculture & Food as described above. Raw samples were delivered to the Ontario Ministry of the Environment, Laboratory Services Branch, Dioxin Analysis Facility in Rexdale, Ontario for processing. Seven replicates of each sample were prepared, each having a sample size of 100 g (wet weight). After samples were prepared, they were stored in a freezer at -10°C until delivery to the analytical laboratories. Frozen samples were hand-delivered to laboratories within a few hours of removing from storage.

Equipment Cleaning Procedures:

All equipment was washed with soap and water, rinsed with distilled water, and then rinsed three times with dichloromethane solvent. A fourth rinse using dichloromethane was collected and analysed by gas chromatography-mass spectrometry (GC-MS) to ensure the absence of PCDD/PCDF or any other contamination. Additional dichloromethane rinses were performed until the GC-MS proving rinse was free of contaminants. All solvents were distilled-in-glass grade.

Sample Homogenization Procedures:

All samples were manually cut into small pieces and homogenized in a blender (Waring Commercial Blender SN598), stainless steel manual meat grinder, or Moulinex coffee grinder purchased new for this study. All apparatus were proven clean before using in similar fashion as described in Section 4.1.1. In addition, a portion of each sample was initially blended by each apparatus used and discarded before homogenization of the remaining sample. Due to the large quantities of each sample to be homogenized, this operation was performed using aliquots of each sample. The ground aliquots were thoroughly mixed by extensive manual stirring in a large pre-cleaned glass beaker. One-hundred gram aliquots of samples were transferred to pre-cleaned amber glass jars and stored in a freezer at -10°C until delivery to the analytical laboratories. Solvent-rinsed aluminum foil was used to line the screw-cap lids of each jar. Specific procedures for each of the samples prepared are described below:

i) Prime beef:

Meat was thawed and manually cut into small pieces. Bones were discarded but fat was not trimmed from the sample. The small pieces were manually ground using a stainless steel meat grinder. All of the ground sample was thoroughly mixed by manual stirring in a glass beaker before removing aliquots for storage in a freezer.

ii) Hamburger:

Ontario beef made into hamburger was received in the form of small meat patties.
Several of these patties were chosen as a grab sample that was manually mixed before sub-dividing into 100-gram replicate samples for analysis. New Zealand boneless beef was received as one large piece of meat which was cut into smaller pieces and ground as described for the prime beef. This sample contained a large proportion of fat which was included in the homogenized sample.

iii) Pork:

Samples of pork were received in the form of frozen pork chops. After they were thawed and manually cut into smaller pieces (bones discarded), the meat was ground using the manual meat grinder.

iv) Chicken:

After being partially thawed, samples of whole chicken were prepared by cutting the breasts, legs, rear, back and neck from the carcass and the remainder was discarded. The skin was retained and was ground with the rest of the sample in the manual meat grinder.

v) Hen eggs:

The contents of eggs were placed in a blender and the shells discarded. Samples were blended until they were homogeneous.

vi) Cow's milk:

No homogenization procedures were needed for samples of milk. Sample components were simply mixed together with gentle manual stirring. These samples were analyzed at the MOE-dioxin laboratory in Rexdale. Other food items described here were analyzed by the Contractor.

vii) Apples:

Several individual apples were composited to give each sample by cutting a large slice from each apple (skin on) and homogenizing the slices in a blender.

Since the blender capacity was not sufficient to contain the entire sample, the process was carried out in batches, and the batches manually mixed together in a large beaker. Cores and stems were not included.

viii) Peaches:

Several slices consisting of about one-third the size of each peach were composited to give each sample. The skin was retained, while the pit was discarded. Slices were blended together until the sample was homogeneous.

ix) Potatoes:

Potatoes were washed using distilled water to remove surface dirt. Slices (skin on) were taken from each of several potatoes for each sample. Slices were manually cut into smaller pieces that were then blended to give a homogeneous paste.

x) Strawberries:

Samples of strawberries were received in cardboard (quart) boxes and frozen until needed. However, improper storage resulted in partial decomposition of the strawberries and samples were discarded. Fresh replacement samples could not be obtained.

xi) Tomatoes:

After removing the stems, tomatoes were manually cut into pieces and the pieces blended until the samples were homogeneous.

xii) Wheat:

Grab-samples were taken from each bag of wheat supplied and ground into fine powder using a Moulinex coffee grinder. Since the capacity of the grinder was not sufficient to contain a complete sample, samples were processed in batches that were manually mixed in a large beaker.

A summary of the samples prepared is given in Table A.4.

A.2.2 Sample Extraction and Analysis: PCDD and PCDF

i) Extraction of Animal Products:

Samples of meat, poultry, eggs were weighed directly into centrifuge tubes equipped with Teflon-lined screw-caps and spiked with 5 ng ^{13}C-2,3,7,8-TCDD and 10 ng ^{13}C-OCDD. The samples were homogenized for 1.5 minutes in a tissue homogenizer after addition of 100 mL acetone:hexane (2:1). The tube was manually shaken prior to and after the addition of 20 mL water, then centrifuged for 5 minutes at 3000 rpm. The hexane was removed and filtered through glass wool into a separatory funnel. Forty mL hexane were added to the centrifuge tube, shaken, and added to the previous hexane extract after centrifugation. Additional hexane was added to the separatory funnel to bring the total volume to about 100 mL. Acetone was removed by gentle shaking of the extract with water, which was discarded.

The extracts were defatted using concentrated sulphuric acid. Gentle mixing of the acid-solvent extract mixture was performed to minimize emulsion formation.

Acid washing was performed until the acid phase was clear and pale yellow. After washing the defatted hexane with water, the solvent extract was passed through anhydrous sodium sulphate and concentrated to 1-2 mL by rotary evaporation. Table A.2 is a list of sample weights extracted.

ii) Extraction of Plant Products:

Samples of fruit and vegetables were weighed directly into centrifuge bottles and spiked with 5 ng ^{13}C-2,3,7,8-TCDD and 10 ng ^{13}C-O$_8$CDD. After addition of 30 g sodium sulphate and 75 mL dichloromethane, the sample was homogenized for 1.5 minutes using a Polytron homogenizer. The extract was centrifuged when necessary to break up emulsions and filtered through sodium sulphate. The extraction was repeated two additional times, using 75 mL volumes of dichloromethane. Ten mL iso-octane were added to the combined extract, which was concentrated to 1-2 mL by rotary evaporations. Table A.5 contains the sample weights (wet weight) extracted.

TABLE A.4 : SAMPLE DESCRIPTION: PHASE II INVESTIGATION OF TOXIC ORGANICS IN FOOD

FOOD TYPE	SOURCE	SAMPLE CODE FOR CONTRACT LABORATORY*
ANIMAL PRODUCTS:		
Pork	East Ontario	PK3, PK4
	West Ontario	PK5, PK6
	Quebec	PK40, PK41
Chicken	Ontario	C7, C8
	Quebec	C9, C10
	U.S.A.	C11, C12
Hamburger	Ontario	H13, H14
	New Zealand	B21, B22
Prime Beef	Ontario	B17, B18
	U.S.A.	B19, B20
Eggs	West Ontario	E21, E22
	East Ontario	E23, E24
	U.S.A.	E25, E26
PLANT PRODUCTS:		
Potatoes	Ontario	PT27, PT28
	P.E.I.	PT29, PT30
	U.S.A.	PT31, PT32
Apples	Ontario	A33, A34
	New York	A35, A36
	B.C.	A37, A38
Tomatoes	Ontario	T39, T40
	U.S.A.	T41, T42
Peaches	Ontario	P47, P48
	U.S.A.	P49, P50
Wheat	Ontario	W51, W52
	Western Canada	W53, W54

* All samples submitted were duplicates without the knowledge of the contract laboratory.

iii) Sample Cleanup:

All concentrated sample extracts were processed through a multi-column cleanup procedure first developed by DOW Chemical Corp (Lamparski and Nestrick, 1980). An initial column consisting of (bottom-to-top) 1.0 g of silica, 2.0 g of 33% 1M NaOH on silica, 1.0 g of silica, 4.0 g of 44% conc. H_2SO_4 on silica, 2.0 g of silica, and a top layer of 1 cm sodium sulphate, was employed. After pre-washing this column with hexane, sample extracts were applied to the column and eluted with about 30 mL hexane. Iso-octane was added to the eluate, which was concentrated to about 1.0 mL.

Extracts were then processed through a second column consisting of 10% silver nitrate on silica. After passing extracts through the column using about 20 mL hexane, the eluate was concentrated by rotary evaporation and solvent exchanged into iso-octane.

The final cleanup column used was 1% water deactivated basic alumina. After a hexane pre-wash, sample extracts were eluted with 12 mL hexane (fraction A) followed by 13 mL 50% dichloromethane in hexane (fraction B). Fraction B, which contained the PCDD/PCDF, was transferred to a conical vial, evaporated to dryness using nitrogen gas, and immediately redissolved in 25 uL iso-octane containing 250 pg/uL triphenylene-d_{12} as an injection standard. All sample extracts were analysed by capillary column high resolution gas chromatography GC-low resolution mass spectrometry (HRGC-LRMS). A procedure blank was processed with each set of samples analysed.

Selected extracts were also analysed by HRGC-high resolution mass spectrometry (HRGC-HRMS) as described later.

TABLE A.5 : SAMPLE WEIGHT (WET WEIGHT) FOR THE DETERMINATION OF PCDD/PCDF IN FOOD

	REPLICATE A		REPLICATE B	
SAMPLE DESCRIPTION	ID#	wt(g)	ID#	wt(g)
East Ontario pork	PK3	11	PK4	8.1
West Ontario pork	PK5	10	PK6	10.3
Quebec pork	PK40	11.8	PK41	13
Ontario chicken	C7	10.9	C8	10.4
Quebec chicken	C9	9.9	C10	10.8
U.S.A. chicken	C11	11	C12	11.8
Ontario hamburger	H13	10.6	H14	9.3
New Zealand hamburger	B21	12.2	B22	12.5
Ontario prime beef	B17	10.3	B18	11.6
U.S.A. prime beef	B19	12.7	B20	12.5
West Ontario eggs	E21	10	E22	10
East Ontario eggs	E23	10	E24	10
U.S.A. eggs	E25	10	E26	10
Ontario potatoes	PT27	52	PT28	50.4
P.E.I. potatoes	PT29	50.2	PT30	51.6
U.S.A. potatoes	PT31	43.4	PT32	50.6
Ontario apples	A33	48.8	A34	48.4
New York apples	A35	39.3	A36	38.8
B.C. apples	A37	40	A38	37.6
Ontario tomatoes	T39	44.3	T40	38
U.S.A. tomatoes	T41	42	T42	43.1
Ontario peaches	P47	47.4	P48	51.1
Ontario wheat	W51	21.2	W52	21.8
Western Canada wheat	W53	30	W54	29.6

iv) Analysis by HRGC-LRMS:

Analysis was performed using selected-ion-monitoring. Three characteristic ions of each PCDD and PCDF congener group (tetra to octachlorinated) were monitored. The GC column used was capable of separating PCDD/PCDF congener groups according to degree of chlorination. Retention times for these groups were determined by analysis of a fly ash extract that contained most PCDD/PCDF congeners. GC-MS analysis conditions are shown in Table A.6.

Quantitation was performed by analysis of an external standard containing one representative isomer for each PCDD and PCDF congener group (tetra to octachlorinated). Data were corrected for the injection standard response and for the percent recoveries of ^{13}C-TCDD and ^{13}C-O$_8$CDD. In cases where no PCDD or PCDF congeners were detected, the instrument response, level of background response and presence of any chemical interferences were taken into account in the estimation of the detection limit for each PCDD/PCDF congener group.

Concentrations were calculated according to the following formula: Concentrations (parts-per-trillion or pg/g)

$$= \frac{A_s.V.C.K.}{A.K_s.W}$$

where:

A_s = area of PCDD/PCDF congener detected in the sample aliquot
A = area of corresponding congener in the external standard mix
V = final sample extract volume (uL)
C = concentration of external standard giving peak area "A" (pg/uL)
K = area of injection standard in the external standard mix
K_s = area of injection standard in the sample aliquot analyzed
W = weight of sample extracted (g)

TABLE A.6 : INSTRUMENTAL CONDITIONS - PCDD/PCDF ANALYSIS

GAS CHROMATOGRAPHY

Injection Mode - on column
Column Flow - He @ 30 cm/sec.
Column - 30M x 0.32 mm DB-5

Oven Temperature Profile

100° - 2 min. -- 220° @ 16°/min.
220° -- 290° @ 12°/min. hold 10 min.
GC/MS Interface - direct couple
Transfer Line Temperature - 270° C

MASS SPECTROMETRY

Ionization Mode - electron impact
Electron Energy - 70 eV
Filament Emission - 0.5 A
Electron Multiplier - 1600 V @ x 10^6 gain
Ionizer Temperature - 170°
Scan - stepped ion MID

A.2.3 Sample Extraction and Analysis: Organochlorine Insecticides and Industrial Chemicals

Plant Products:

Fruit and vegetable homogenate was sub-sampled and extracted using the following procedures.

Fifty grams of sample were blended with 200 mL of 2:1 acetonitrile-water and filtered. A 25 g sample aliquot was removed, diluted with 500 mL water and 25 mL saturated sodium chloride solution, and partitioned with 2 x 50 mL dichloromethane. The dichloromethane was dried by percolation through anhydrous Na_2SO_4. Hexane was added and the extract was concentrated just to dryness using a rotary vacuum evaporator. The residue was re-dissolved in 5.0 mL hexane.

A portion of the concentrated sample (4.5 mL) was cleaned up and fractionated for organochlorine insecticides according to the procedure of Mills *et al*. (1972) and Frank *et al*. (1975).

Animal Products:

Ten gram sub-samples of meat and egg homogenate were mixed thoroughly with anhydrous sodium sulphate and exhaustively extracted with hexane in a Soxhlet apparatus, followed by removal of the solvent by rotary evaporation. Subsamples of fluidized fat (1.0 g) were then cleaned up according to the procedure of Frank *et al*. (1975). PCBs were fractioned from the organochlorine insecticide according to the procedures of Berg *et al*. (1972) and Holdrinet (1974).

Gas chromatographic determination of organochlorine pesticides and contaminants were made on 1.8 m x 3 mm i.d. columns packed with 1.5%

OV-17/2.0% OV-210 on 100-120 mesh Gas Chrom Q and with Ni electron capture detectors operated in the constant current mode.

Detection limits were about 1 ug/kg (1 ppb) in egg fat for organochlorine insecticides and 10 ug/kg (10 ppb) for PCB. PCB were identified and quantitated by comparison with mixtures of Aroclors 1254 and 1260 and by checking for resemblance to peaks VII, VIII and X according to the system of Reynolds (1971).

APPENDIX B

Health and Welfare
Canada

Health Protection
Branch

Tunney's Pasture
Ottawa, Ontario
K1A 0L2

October 28, 1987

Ms Beverley Hanna-Thorpe
Ministry of the Environment
Hazardous Contaminants Branch
40 St. Clair Avenue West, 7th Floor
Toronto, Ontario, M4V 1M2

Dear Beverley,

OMAF/MOE Toxics in Foods Committee

With regard to data generated by Health Protection Branch on PCDDs and PCDFs in foods for the use by the above committee, we can report the following.

In 1985 the Food Research Division initiated a total diet program whereby foods purchased in local markets were composited in the laboratory to approximate an average diet by consumers. Some 33 of these samples have been analyzed in the last year for all the tetra- to octa-CDDs and -CDFs. A summary of these results are enclosed in the accompanying table.

Generally, using the sample size as reported, we are unable to detect any tetra- or penta-CDDs or any PCDFs in these foods. In certain samples, mainly eggs and pork, we can find small amounts (1 to 50 ppt) of the hexa-hepta- and octa-CDDs. These results support our original contention that these contaminants, if present, are usually found in animal foods of high fat content and then only in small amounts. Levels that have been reported in the Davis report (over 1000 ppt) are not encountered.

We are presently modifying our methodology to obtain better detection limits in foods (down to 0.1 ppt on a fat basis) since recent results from Germany show levels of 0.2 to 2 ppt of many 2378-substituted PCDDs and PCDFs in cow's milk, butter and pork. I think you will agree that, for the purpose of food exposure, it is better to work with an actual number no matter how small rather than non-detectable values.

I trust you can use these results in the Committee's final report.

Sincerely,

J.J. Ryan, Ph.D.
Food Research Division

Encl.

PCDDs and PCDFs in total diet samples analysed by Health Protection Branch in 1986-87; values in pg/g on a whole weight basis unless otherwise noted.

Food Type	No. Samples	Sample Size	Content
Fruit (apple, pear)	2	90 g	all ND[1] (0.5)
Fish (fresh, salt)	2	5.0 g	all ND (1)
Eggs white	2	25-30 g	all ND (0.5 to 2)
yolk	2	8-14 g	H_6CDD-ND & 5.9; H_7CDD-5.9 & 9.5; OCDD-57 & 41
whole	2	9.0 g	H_6CDD-ND (2); H_7CDD-ND & 3.1 (679) plus 5.7 (678); OCDD-18 & 44
Poultry	2	5.9 g	all ND (2 to 5) except OCDD, ND (10)
Beef ground	1	5.0 g	H_7CDD-6.2 & OCDD-12
organ meat	1	5.0 g	all ND(1) except OCDD,ND (5)
steak	2	5.0 g	all ND(2) except OCDD,ND (10)
Lamb	1	5.0 g	all ND (1 to 5)
Pork fresh	1	5.0 g	H_6CDD-1.1; H_7CDD-1.8 (679) & 1.8 (678); OCDD-9.8
cured	2	5 & 9 g	H_6CDD-ND; H_7CDD-1.6 & 2.6; OCDD-4.4 and 15
cold cuts	1	5.0 g	H_7CDD-3.1; OCDD-7.8
Milk (whole)	4	70-150 mL	all ND (0.1 to 2 ppt whole milk basis) except 1 sample - H_7CDD-0.15 & 0.28 (11 & 20 on fat basis) OCDD-1.0 (20 on fat basis)
2% substitutes	1	125 mL	all ND (0.1 to 0.35)
	2	75-100 mL	all ND (0.2 to 0.3)
Butter	1	2.7 g	H_7CDD-7.6; OCDD ND (20)
Cheese	1	5.0 g	all ND (2 to 10)
Margarine	2	2.7-3.0 g	all ND (2 to 4) except OCDD-10
Vegetable fat	1	2.7 g	all ND (2 to 5) except OCDD-ND (10)

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[1] - non-detected followed by bracketed detection limits in parts per trillion (ppt; pg/g)

APPENDIX C

ONTARIO MINISTRY OF THE ENVIRONMENT ANALYSIS OF APPLES, MILK AND ANALYSIS OF COMPOSITE FOOD EXTRACTS FOR PCDD AND PCDF AND TO ACHIEVE LOWER DETECTION LIMITS

C.1 BACKGROUND

Upon release of the findings of a Toronto Department of Health investigation of trace organics in food, in which significant levels of PCDDs and PCDFs were detected in composite food samples, analysis of Ontario apples and milk composite samples was immediately initiated. Apples and milk were chosen because the Department of Health study found that the greatest levels of PCDD/PCDF contamination were in a fruit composite sample consisting of 70% apples by weight and in a sample of milk.

The Ontario Ministry of Agriculture and Food (OMAF) collected samples for analysis by the Ontario Ministry of Environment (MOE) dioxin laboratory in Rexdale.

A subsequent study was made to determine the lowest detection limits achievable for samples of Ontario food by combining extracts from replicate samples and re-analysing them under optimum instrumental conditions.

C.2 EXPERIMENTAL PROCEDURES - APPLES AND MILK

C.2.1 Sample Preparation and Extraction:

Apples were manually cut into small pieces (peel on, core removed) and placed on the surface of pre-cleaned metal foil to dry for three days. The dried sample weights were about 10% of the initial wet weight. Ten gram aliquots (dry weight) were chosen for overnight (ca. 16 hour) extraction by Soxhlet apparatus using 200 mL distilled-in-glass grade toluene. Some mold formation occurred during sample drying. Before extraction, samples were spiked with 10 ng ^{13}C-2,3,7,8-TCDD and 20 ng ^{13}C-OCDD.

Twenty-gram aliquots of composite milk samples were weighed directly into Erlenmeyer flasks and 70 mL concentrated hydrochloric acid were added to each sample. Milk samples were then spiked with 10 ng ^{13}C-2,3,7,8-TCDD and 20 ng ^{13}C-OCDD and were mixed by shaking for one hour using a wrist-shaker. Extractions were performed by shaking overnight with 70 mL distilled-in-glass grade hexane solvent. Emulsions that formed in some samples were easily broken-up by placing sample flasks in an ultrasonic bath and agitating for 10 minutes.

C.2.2 Sample Extract Clean-up and Analysis:

Multi-layer cleanup columns containing silica, 44% H_2SO_4 on silica, and 22% NaOH on silica, were used to remove interfering co-extractives. A second stage dual-column containing $AgNO_3$ (top column) and activated alumina (bottom column) were also employed. Concentrated and cleaned-up extracts were analyzed by gas chromatography-mass spectrometry (GC-MS). Quantitation was performed by external standards prepared by direct weighing of pure crystals. Correction for analyte losses through sample preparation was made by adjusting results for recoveries of the isotopically-labelled 2,3,7,8-TCDD and OCDD standards added to the samples before extraction.

C.2.3 Results and Discussion

Table C.1 shows the results from the GC-MS analysis of Ontario apples and Ontario milk composite samples for PCDD/PCDF. None of these contaminants were found in the composite milk samples, while only OCDD was detected in samples of apples. Because the apple data are based upon dry weight, the concentrations of OCDD and detection limits shown for the two apple samples are about ten times lower in the original whole apple samples. This contrasts with the results shown in Section 4.1 which are expressed on a fresh weight, not a dry weight, basis.

TABLE C.1 : ONTARIO MINISTRY OF ENVIRONMENT ANALYSIS OF APPLE* AND MILK SAMPLES FOR PCDD AND PCDF (All data parts-per-trillion; ppt, 10^{-12} g/g)

	APPLE	APPLE	MILK COMPOSITE SAMPLES			
PCDD	#2355	#2356	WESTERN	EASTERN	NORTHERN	CENTRAL
T_4CDD	ND(2)	ND(2)	ND(2)	ND(2)	ND(2)	ND(5)
P_5CDD	ND(2)	ND(2)	ND(2)	ND(2)	ND(2)	ND(5)
H_6CDD	ND(2)	ND(2)	ND(4)	ND(2)	ND(2)	ND(6)
H_7CDD	ND(2)	ND(2)	ND(5)	ND(3)	ND(3)	ND(8)
O_8CDD	46	7	ND(8)	ND(5)	ND(5)	ND(10)
Total	46	7	ND	ND	ND	ND
PCDF						
T_4CDF	ND(2)	ND(2)	ND(2)	ND(2)	ND(2)	ND(5)
P_5CDF	ND(2)	ND(2)	ND(2)	ND(2)	ND(2)	ND(5)
H_6CDF	ND(2)	ND(2)	ND(4)	ND(2)	ND(2)	ND(6)
H_7CDF	ND(2)	ND(2)	ND(4)	ND(3)	ND(3)	ND(6)
O_8CDF	ND(2)	ND(2)	ND(4)	ND(5)	ND(5)	ND(8)
Total	ND	ND	ND	ND	ND	ND
% Recoveries						
T_4CDD	110	170	170	110	170	56
O_8CDD	290	330	120	55	85	83

ND-not detected, detection limit in brackets (ppt)
All data corrected for percent recovery of surrogate standards

* apple data based on dry weight

C.3 ANALYSIS TO ACHIEVE LOWER DETECTION LIMITS

C.3.1 Analysis of Composite Food Extracts:

To achieve lower detection limits in samples of the Ontario foods described in Section 4.1 and C.2, replicate samples were combined where feasible. These were then concentrated to a small sample volume (4-6 uL) and analysed by HRGC-HRMS after cleaning the mass spectrometer ion source and optimizing for high sensitivity analysis at nominal resolution 12,000. Eight blanks prepared during the original analysis of these samples were also combined and concentrated for re-analysis.

The following Ontario food samples were combined: hamburger and prime beef samples H13, H14, B17, B18; pork samples PK3, PK5, PK6; chicken samples C7, C8; egg samples E21, E22A, E22B, E23 (note: E22A, E22B are replicates); four composite milk samples from previous work; apple samples A33, A34; peach samples P47, P48, and wheat samples W51, W52. In addition, tomato sample T40 and potato sample PT28 were re-analysed. These two samples were not combined with their replicates because the replicates contained known interferences for T_4CDF and P_5CDF analysis.

C.3.2 Results and Discussion:

By combining extracts and analysing them under optimized HRGC-HRMS conditions, average detection limits were lowered by about a factor of 10. In some cases, contaminants were found at levels below the detection limits previously achieved from analysis of individual samples. However, the data shown in Table C.2 generally confirms the absence of significant levels of dioxins/furans from Ontario food products at these lower detection limits. The code BC (blank contamination) has been used to report concentrations of OCDD and OCDF because these compounds were found in the combined blank extract at levels corresponding to approximately the same concentrations as found in the composited food samples.

For some samples, T_4CDF and P_5CDF interferences were detected (chlorinated diphenyl ethers) that were present in the original extracts prepared by the contractor. Although these interferences were largely eliminated by additional cleanup of the extracts, traces were still detected in some samples at the lower detection limits achieved. These interferences were also observed in the composite blank analysis.

TABLE C.2 : ANALYSIS OF COMPOSITED ONTARIO FOOD SAMPLES FOR PCDD AND PCDF*

FOOD COMPOSITE	BEEF	PORK	CHICKEN	EGGS	MILK	APPLES	PEACHES	WHEAT	TOMATOES	POTATOES
TOTAL SAMPLE WEIGHT(g)	41.9	31.4	21.2	40	82.6	97.2	98.5	42.8	38	50.4
T_4CDD	ND(0.4)	ND(0.1)	ND(1)	ND(0.1)	ND(0.05)	ND(0.2)	ND(0.06)	ND(0.4)	ND(0.07)	ND(0.8)
P_5CDD	ND(0.1)	ND(0.08)	ND(0.2)	ND(0.1)	ND(0.01)	ND(0.01)	ND(0.06)	ND(0.1)	ND(0.03)	ND(0.6)
H_6CDD	ND(0.4)	ND(0.03)	ND(0.06)	ND(0.07)	ND(0.01)	ND(0.07)	ND(0.1)	ND(0.2)	ND(0.02)	ND(0.2)
H_7CDD	2^2	1.3^2	0.03^2	0.8^2	0.4^2	ND(0.02)	ND(0.02)	ND(0.05)	ND(0.04)	ND(0.07)
O_8CDD	BC(10)	BC(9)	BC(30)	BC(5)	1	BC(1)	BC(1)	BC(0.9)	BC(0.6)	BC(2)
T_4CDF	INT(5)	ND(0.3)	INT(3)	ND(0.2)	ND(0.01)	INT(5)	INT(10)	INT(40)	INT(3)	ND(2)
P_5CDF	ND(0.1)	ND(0.05)	ND(0.4)	ND(0.06)	ND(0.01)	INT(2)	INT(6)	INT(10)	INT(2)	ND(0.3)
H_6CDF	2.4^3	0.2^1	2.7^1	0.9^1	1^2	ND(0.01)	ND(0.03)	ND(0.2)	ND(0.02)	ND(0.01)
H_7CDF	1.4^2	0.06^2	3.1^2	2^3	0.5^2	ND(0.001)	ND(0.005)	ND(0.02)	ND(0.01)	ND(0.02)
O_8CDF	BC(0.6)	BC(2)	BC(4)	BC(2)	0.2	BC(0.1)	ND(0.03)	ND(0.4)	ND(0.02)	ND(0.03)

*All data parts-per-trillion (ppt: 10^{-12}g/g), corrected for internal standard recovery
ND: not detected. Values in brackets are detection limits (ppt)
BC: blank contamination. Value detected (brackets) may be from contamination of sample
INT: interference observed, analytes may be present at concentrations below those given
Superscripts are number of isomers observed.

APPENDIX D

CRITERIA FOR INTERPRETING PCDD and PCDF ANALYTICAL DATA IN FOOD BASKET SURVEY INVESTIGATION (March 1987)

D.1.0 INTRODUCTION

A joint investigation was initiated by the Ontario Ministries of Agriculture and Food (OMAF) and Environment (MOE) to provide an increased data base of PCDD/PCDF in food basket items. This study was designed to incorporate comprehensive quality control (QC) measures including replicate analyses, inter-laboratory comparison, and analysis of frequent procedure blanks. As part of the QC program, methods were developed prior to sample analysis. These methods are described in this appendix.

The objectives of developing such rules are to ensure that:

- a high degree of reliability can be attached to analytical data;
- data reported by different laboratories can be compared on a common basis; and
- the methods of data treatment are clearly specified.

The problems of data interpretation of ultra-trace analysis are complex. Principal considerations for ppt level determination of PCDD/PCDF in food include the following:

1. With what reliability can an instrumental response be attributed to the presence of a PCDD/PCDF congener?
2. In what terms can the above qualitative reliability be expressed?
3. With what reliability can a detected PCDD/PCDF congener be attributed to a real presence in the sample compared to background levels?

4. In what terms can the above qualitative reliability be expressed?
5. Do the analytical quality control procedures support the reporting of quantitative PCDD/PCDF levels detected in samples?
6. To what extent are the differences observed between samples from the same source induced by either the analytical process or field operations, compared to real environmental changes?

To deal with the above issues quantitatively requires application of statistical procedures to real monitoring data, however, there is currently no large database available that would enable such an analysis to be performed. In addition, an important facet in establishing accuracy is the existence of a number of independent analytical facilities which can confirm each other's findings. To date, only a few laboratories in the world have the compatability to perform analysis on major food contaminants for PCDD/PCDF. Therefore, important considerations of this work are the interpretation protocols used to assess raw analytical data and to report PCDD/PCDF concentrations with reliability commensurate with the current analytical state-of-the- art.

The following protocols were developed specifically for interpretation of results from the determination of PCDD/PCDF at ppt levels in food basket samples. As the database for this application is expanded, it may be possible to restate these interpretation criteria on a statistical basis, rather than the empirical rules that follow. Because special problems of data interpretation can arise on a case-by-case basis, these rules may require further modification. All special interpretation problems and improvements to the following protocols were fully documented.

D.2.0 DATA INTERPRETATION CRITERIA FOR FOOD BASKET SURVEY FOR PCDD/PCDF

The principal variables in data interpretation for quantitative analysis are significantly affected by the quality control procedures associated with a specific method. For the determination of PCDD/PCDF compounds using GC-MS these factors are the daily instrument calibration, determination of the recovery of isotopically labelled internal standards added prior to extraction, and analysis of procedure blanks. For the highest degree of quality control, replicate determinations of some samples is an important additional step.

PCDD/PCDF peaks which are detected can be classified as those present in trace concentrations for which a reliable numerical value cannot be determined, and those for which numerical values will be reported. For the purpose of this report, the term Quantitation Limit (QL) will refer to the concentration above which a high reliability can be given to numerical values. Peaks detected at levels below QL are trace values at which reduced confidence can be given to the accuracy of reported concentrations. Important factors that affect the value of QL are the method detection limit (DL) and recovery correction procedures.

D.2.1 Detection Limit (DL):

The DL can be calculated for each CDD/CDF congener group in all samples and procedure blanks as follows:

$$DL_i = \frac{N_Q \; S_i \cdot V_f}{N_i \cdot R_{4,8} \cdot V_s \cdot V_i}$$

Where: N_i:1 = S:N of GC-MS peak of the quantitation ion for congener ($_i$) in the daily standard calibration.

N_Q:1 = S:N of GC-MS peak of the quantitation ion for congener ($_i$), if the least abundant characteristic ion monitored is present at S:N = 3:1.

S_i = picograms of standard congener ($_i$) injected into GC-MS in the daily standard calibration.

$R_{4,8}$ = recovery of appropriate isotopically labelled internal standard, expressed as a fraction where 100% recovery = 1.0.

V_i = volume of sample injected into the GC-MS, generally 1-2 uL.

V_s = sample weight before extraction (grams, wet weight basis).

V_f = final sample volume (uL).

When all of the above terms are expressed in the units shown, DL is in parts-per-trillion. The validity of this calculation should be confirmed periodically by analysis of standards at concentrations no greater than 2-3 times DL for each PCDD/PCDF congener.

To determine S:N of peaks, the average noise level is first determined. This can be envisioned by the location of a line drawn through the fluctuating noise so that the total area of peaks above the line is equal to the area below the line, if the baseline of peaks is drawn at the lowest peak valley. The height of the noise is taken from the average noise line to the top of the largest noise fluctuation (excluding noise spikes).

Peaks detected at a height of three times this value have S:N = 3:1. The factor of N_Q in the numerator of the previous expression corrects the S:N of the quantitation ion from the external standard to the S:N it would have at the instrumental detection limit. This value is not 3 because these criteria require all characteristic PCDD/PCDF masses monitored to be present; and if the S:N of the least abundant ion monitored is 3:1, then the S:N of the quantitation ion will be greater than 3:1.

D.2.2 Recovery Correction:

The isotopically labelled internal standards (^{13}C-2,3,7,8-TCDD and ^{13}C-O_8CDD) used for recovery correction are quantitated using external standards. Native T_4CDD and P_5CDD congeners are corrected for recovery of ^{13}C-2,3,7,8-TCDD, while the H_7CDD and O_8CDD congeners are corrected for ^{13}C-O_8CDD. The H_6CDD congeners are adjusted for the average recovery of ^{13}C-2,3,7,8-TCDD and ^{13}C-O_8CDD.

Quantitative data are suspect when recoveries are lower than the range generally achieved, and can not be reported without indication of this fact. Concentrations can not be corrected for recovery if the appropriate surrogate recovery is less than 20%. When surrogate recovery is below 20% but no CDD/CDF congeners are detected, the detection limits can still be corrected for recovery as described above.

If only the ^{13}C-2,3,7,8-TCDD recovery is below 20% then data for only H_6CDD, H_7CDD, and OCDD congeners can be corrected (for ^{13}C-O_8CDD recovery). Conversely, if ^{13}C-O_8CDD recovery is too low, then only T_4CDD, P_5CDD and H_6CDD congeners can be corrected (for ^{13}C-2,3,7,8-TCDD recovery). Concentrations uncorrected because of low surrogate recovery should be reported to one significant figure.

Recovery correction is applied to recoveries up to 120%. Data for samples where recoveries are above this value can be reported uncorrected and given to one significant figure. Detection limits can also be reported uncorrected when surrogate recoveries are above 120%.

D.2.3 Quantitative Limit (QL):

That level at which a relatively high degree of reliability can be placed on a numerical result is referred to in this report as the quantitation limit (QL). Peaks detected at lower levels than QL are qualified by reporting their concentrations to one significant figure and by showing the detection limit for this determination in brackets. Trace data are presented in this manner to indicate the difficulty of assigning a numerical value at levels close to the method detection limit.

QL is assigned to each PCDD/PCDF congener for each sample. Its value is three times DL, where DL is calculated as described above.

D.2.4 External Standard Quantitation:

Quantitative determinations are performed by comparing peak responses (areas or heights) in the sample with those of a standard mixture that contains one representative PCDD and PCDF compound from each group of tetrachlorinated to octachlorinated congeners. Numerical concentrations are calculated using the following formula:

$$X(\text{ppt}) = \frac{A_x \times V_f}{RF_{4-8} \cdot V_i \cdot V_s \cdot R_{4,8}}$$

Where:

X = is the concentration in parts-per-trillion (ppt)

A_x is the measured GC-MS peak area of X

V_f is the final volume of sample after extraction and concentration, in microliters (usually 10 uL)

V_i is the volume of sample injected into the GC-MS, generally 1-2 uL

V_s is the sample weight extracted (grams)

R_{4-8} is the recovery of either ^{13}C-2,3,7,8-TCDD or $^{13}C-O_8CDD$, or the average of these two recoveries (see recovery correction protocol), expressed as a fraction where 100% recovery = 1.00

$RF_{4,8}$ is the response factor of the appropriate representative congener in the external standard, in GC-MS peak area per picogram injected

D.2.5 Determination of 2,3,7,8-TCDD:

Isomer-specific analysis of 2,3,7,8-TCDD is performed by use of a GC capillary column that is capable of separating this isomer from a mixture of all 22.

D.2.6 Isomer Patterns:

In addition to the quantitative data for PCDD/PCDF in replicate determinations, the patterns of various PCDD/PCDF isomers/ congeners detected are important measures of data quality. For replicate determinations, these patterns must match closely.

All of the above factors are taken into account when interpreting the raw GC-MS data from analysis of the food basket samples. The reporting of quantitiative data depends upon DL, QL, percent recoveries, results of procedure blanks, and results of replicate determinations as specified in the following criteria (A-D).

A. Peaks identified as PCDD/PCDF congeners from GC-MS analysis must satisfy the following criteria:

   1) Signal to Noise ration (S:N) must be greater than or equal to 3 to 1 (3:1) for the least abundant characteristic ion monitored.

   2) Isotope ratios for the characteristic ions monitored must be within ±15% of values determined from an external standard analyzed the same day.

   3) Retention times of peaks identified by 1) and 2) must be within known retention windows of the appropriate PCDD/PCDF congener group.

   4) GC peak widths must be at least 2 seconds wide at 1/2-height to ensure discrimination against noise spikes.

   5) Congeners detected by LRMS techniques according to 1) - 4) may be confirmed by HRMS analysis at resolution of about 10,000. Peaks detected by HRMS analysis are those which satisfy criteria 1) to 4).

B. For each PCDD/PCDF congener group in each sample, DL is calculated as described previously. Trace level data, and data for samples where surrogate recoveries are high or low, is qualified.

C. For quantitative data to be reported, PCDD/PCDF congeners must be detected in both replicate samples. Where data are not available in one replicate an additional replicate from storage will be analyzed. If any congener is detected in only one replicate, the code NR(X) (not replicated) is reported, where X is the concentration determined in the sole replicate.

Where replicate analyses are performed, the average of the two analyses is reported.

D. For any PCDD/PCDF congener detected in both sample and procedure blank for that sample, the code BC(X) (blank contamination) is used, where X is the concentration determined in the sample. Data from blanks is reported as well. However, if the levels found in the sample are at least 10 times greater than found in the blank, sample concentrations are reported without the code BC. The Table of Results should indicate that low-level blank contamination was detected.

E. Samples where PCDD/PCDF are detected after applying the above criteria may be analyzed by an external laboratory to ensure quantitative accuracy.

D.3.0 SUMMARY OF INTERPRETATION CRITERIA

For the food basket PCDD/PCDF survey, all reported concentrations have gone through a strict quality control procedure designed to ensure the elimination of false positive results. Data for samples where blank contamination was found, recoveries were outside expected values or where results could not be replicated are suspect and are not reported without explanation. By applying these strict criteria, the reliability of identification and quantitation of PCDD/PCDF congeners is high.

APPENDIX E

A REVIEW OF ONTARIO-OMAF STUDIES OF RESIDUES OF PERSISTENT ORGANOCHLORINE PESTICIDES AND INDUSTRIAL CHEMICALS IN ONTARIO FOODS AND TOBACCO

E.1.0 INTRODUCTION

This appendix addresses the following current issues, that pertain to persistent toxic compounds:

i) Residues of persistent organochlorine pesticides in food arising from past and current uses in agriculture;

ii) Residues of persistent organochlorine pesticides in food and tobacco resulting from persistent residues in soils;

iii) Residues of persistent organochlorine compounds in foods arising from industrial activities; and

iv) Residues of persistent organochlorine pesticides in foods related to non-agricultural use of pesticides.

E.2.0 REVIEW OF OMAF STUDIES

E.2.1 Persistent Organochlorine Insecticides Used in Agriculture

Throughout the 1960's monitoring data were accumulated that indicated persistent organochlorine pesticides were increasingly present in fatty tissues of domestic farm animals. These residues were frequently shown to be in violation of health standards for meats, eggs, milk and other animal products.

Monitoring surveys were carried out by OMAF between 1967-69 that involved 1651 bulk tankers delivering milk to 286 dairies in the province (Frank *et al*. 1970). Twenty-two bulk tankers or 1.3% were found hauling milk, that had residues in violation of the *Food and Drugs Act and Regulations* (1986).

TABLE E.1 : RESIDUES OF ORGANOCHLORINE INSECTICIDES AND INDUSTRIAL CHEMICALS IN MEATS, MILK AND EGGS (FRANK ET AL. 1985A, B: FRANK, BRAUN AND FLEMING 1983).

ANIMAL PRODUCT	YEARS	SAMPLES (CARCASSES)	MEAN RESIDUE IN EDIBLE FAT (ng/g)							
			CHLORDANE	DDT	DIELDRIN	ENDOSULFAN	HCB	HCH	HE	PCB
Beef	1969-70	137 (835)	1	123	33	0.1	10	16	1	239
	1975-76	21 (53)	1	44	23	<0.1	NM	32	3	145
	1981-[1]	197 (990)	1	4	6	0.4	<2	3	4	5
	1986-86	20	<1	<5	<2	<0.1	<2	<2	<1	<5
Pork	1969-70	35 (170)	<1	187	12	<0.1	NM	30	<1	330
	1973-74	5 (18)	<1	41	2	<0.1	2	NM	<1	24
	1981	38 (190)	<1	5	<2	<0.1	NM	41	<1	3
	1985-86	20	<1	<5	<2	<0.1	<2	<2	<1	<5
Poultry	1969-70	19 (95)	NM	391	28	NM	NM	9	<1	946
	1975-76	9 (30)	22	139	20	10	9	<1	6	391
	1981-82	50 (180)	5	2.3	<2	1.5	<0.1	1	5	5
	1985-86	45		<5	3	<0.1	<0.1	3	<1	<5
Cow's Milk	1970-71	337	<1	125	35	<0.1	5	<1	<1	85
	1973	350	<1	51	15	<0.1	7	<1	<1	115
	1977	380	<	15	11	1	0.2	NM	4	35
	1983	359	0.3	12	6	0.4	0.7	9.3	4	24
Hen Eggs	1969-70	30 (120)	NM	188	8	<0.1	NM	5	<1	405
	1973-74	22 (64)	<1	137	11	<0.1	108	<1	<1	255
	1981-82	51 (101)	<1	4	<0.5	<0.1	0.6	<1	<1	10

NM - Not measured

[1] Fenthion identified in 7/197 samples, 171 ± 256 ng/g

HE = heptachlor epoxide, HCH = hexachlorocyclohexane, HCB = hexachlorobenzene

TABLE E.2 : DECLINING ORGANOCHLORINE RESIDUES AS OBSERVED BY THE INCREASING FREQUENCY OF RESIDUE LEVELS BELOW 10 ng/g IN THE FAT OF THE TISSUE (FRANK ET AL. 1985 A & B)., FRANK, BRAUN AND FLEMING, 1983).

ANIMAL PRODUCT	YEARS	CHLORDANE	% SAMPLES BELOW 10 ng/g DDT	DIELDRIN	ENDOSULFAN	HCB	HCH	HE	PCB
Beef	1969-70	100	0.8	10.2	100	50	73.0	96.9	0.0
	1975-76	100	9.6	66.7	100	NM	85.7	100	9.5
	1981	100	73.1	92.9	100	100	97.5	97.4	78.2
	1985-86	100	100	100	100	100	100	100	100
Pork	1969-70	100	0.0	82.9	100	NM	85.7	100	0.0
	1973-74	100	18.7	100	100	100	1001	100	18.8
	1981	100	92.1	100	100	NM	81.1	100	92.1
	1985-86	100	100	100	100	100	100	100	100
Poultry	1969-70	NM	0.0	21	NM	NM	90	95	0.0
	1975-76	100	22.0	33	94	80	100	89	0.0
	1981-82	100	100	100	100	100	100	96	84
	1985-86	100	100	100	100	100	95.6	100	100
Cows Milk	1970-71	100	0.0	0.0	92.4	100	98.2	97.0	0.0
	1973	100	3.5	9.0	100	81.2	100	97.5	0.0
	1977	98.4	49.0	59.1	99.4	97.5	100	99.0	13.6
	1983	99.7	69.4	95.3	99.4	100	93.3	99.7	95.6
Hen Eggs	1969-70	NM	40.0	67.0	100	NM	82	100	0.0
	1973-74	100	44.0	73.0	100	30	100	100	3.0
	1981-82	100	100	100	100	100	100	100	50

NM = not measured
HE = heptachlor epoxide, HCH = hexachlorocyclohexane, HCB = hexachlorobenzene

Analytical results indicated that 17 tankers had dieldrin residues and one tanker had heptachlor epoxide residues in milkfat above the allowable 0.1 ug/g, and three had DDT residues above the permitted 1 ug/g and one had lindane residues in milkfat above the 0.2 ug/g limit.

At the same time a further 212 or 12.5% of the tankers contained milk with residues below the actionable levels but of concern to health officials. In all cases, except for lindane, the insecticides had been used on food or fodder crops or on timber and was introduced to the farm unknowingly by the owners of the dairy herds.

In 1969, Ontario banned all agricultural uses of aldrin, dieldrin and heptachlor. In 1970 the use of DDT was restricted to use by permit and all outdoor uses were banned in late 1971. Other persistent organochlorine insecticides (OCI) were removed from use by federal and/or provincial actions during the early 1970's.

Monitoring programs were set up to follow the decline of terminal residues in meat, eggs and milk and these studies are continued to the present day. A summary of the findings appear in Tables E.1 and E.2.

Monitoring 2102 milk samples since 1970 has not revealed further violations by organochlorine insecticides (OCI). In fact, the data have shown a marked decline in the average OCI residues and a substantial increase in the percent of samples that has fallen below 0.01 ug/g (Table E.3).

Between 1969 and 1986, 764 samples of meat were analysed for both organochlorine and organophosphorus insecticides and only six samples have been found to be in violation. Two each involved DDT, dieldrin and fenthion (Table E.2).

None of the persistent organochlorine insecticides listed as having been detected, with the exception of HCH, were used on domestic animals. Even the HCH residue which was made up of three isomers did not all come from topical applications; only lindane, the gamma isomer is still permitted for use on livestock, although a 30 day waiting period after application is required before slaughter.

TABLE E.3 : VIOLATION OF PESTICIDES IN MEAT AND MILK 1969-86 (FRANK ET AL 1983, 1985 A AND B)

ANIMAL PRODUCT	TOTAL SAMPLES ANALYSED	VIOLATIONS	YEAR	PESTICIDE	RESIDUE (ug/g)	MRL (ug/g)
Beef	505	1	1970	DDT	11.3	7.0
Pork	122	1	1981	fenthion	0.6,0.4	0.1
Poultry	137	1	1971	DDT	7.7	7.0
Hen Eggs	118	2	1970,71	dieldrin	0.7,0.4	0.25
Cow's Milk	2021	0				

E.2.2 Soil residues of persistent OCI in tobacco and food

Persistent organochlorine insecticides were used in the production of tobacco up to 1969 when the registration of aldrin, dieldrin, and heptachlor were cancelled for this use. In 1970 DDT was restricted and in 1971 the use of DDT and endrin were cancelled. In 1978 chlordane and endosulfan were deregistered. The decline in the OCI residues in tobacco for the period 1970 to 1985 is shown in Table E.4. Residues of replacement pesticide compounds are also given in this table. Many of the insecticides which are now being used leave no detectable residues.

TABLE E.4 : PESTICIDE RESIDUES IN FLUE-CURED TOBACCO FROM 34 FARMS BETWEEN 1970-85 (FRANK ET AL, 1987)

Pesticide	Residues (ug/g) in dried cured tobacco leaf				Last year of use
	1970	1975	1980	1985	
t-DDT (I)	1.83	0.89	0.62	0.57	1971
Dieldrin (I)	0.080	0.035	0.081	0.027	1969
Endrin (I)	0.11	0.06	0.018	0.067	1970
Heptachlor epoxide (I)	0.023	0.018	0.017	0.003	1969
Chlordane (I)	<0.001	0.076	0.008	0.004	1978
t-Endosulfan (I)	3.67	3.19	0.081	0.005	1978
Lindane (I)	<0.001	0.010	0.005	0.008	-
Permethrin (I)	-	-	0.39	0.012	-
Chlorpyriphos (I)	<0.005	<0.005	<0.005	<0.005	-
Acephate and methamidophos (I)	-	-	0.105	0.010	-
Metalaxyl (F)	-	-	0.36	<0.010	-
Diphenamid (H)	-	-	0.68	0.19	-

E.2.3 Residues of Industrial Chemicals in Food

Not all chemical residues found in food occur as a result of agricultural use. Residues of HCB and PCB that have appeared in food originated from their release to the environment by urban and industrial activities. Other substances which were not used in agriculture have caused concern as potential food contaminants. These include (i) polybrominated biphenyls (PBB), a serious accidental contaminant in domestic animal feed which subsequently resulted in contaminated meat in Michigan but did not appear in Ontario-grown produce, (ii) mirex, an industrial chemical, manufactured in the United States, but not in Canada entered Lake Ontario and was found in fish but did not appear in agricultural produce in Ontario, and (iii) polychloronaphthalenes which appeared in wildlife tissues and were suspected in food commodities at trace levels.

During the 1970s, the detection of PCB residues was found to be ubiquitous in meats, eggs and cow's milk (Tables E.1 and E.2). Recent analyses have shown a marked decline in these residues. The highest mean residues were observed in poultry meat at 946 ng/g in 1969-70, and these levels had declined to less than 5 ng/g by 1985-86. At the same time, the percentage of samples exceeding 10 ng/g decreased from 100 to 0%. Actionable residues under the Food and Drugs Act and Regulations were set at 0.1 ug/g for the fats of meat and eggs and 0.2 ug/g for milk fat. The results of monitoring programs appear in Table E.2 and reveal that a high percentage of samples exceeded these levels in 1969 - 70 but by 1985 - 86 all meat fat samples were below this level. The above findings are in keeping with the actions carried out since 1971.

A survey of fruit and vegetables in 1986 found no detectable PCB residues (Frank *et al*., 1987a,b. Unpublished data).

In 1971 a voluntary action was agreed upon in North America whereby PCB in all open system uses would be phased out of use by the manufacturers. By 1976 U.S.

TABLE E.5 : PCB RESIDUES ABOVE 0.1 ug/g IN FATS OF MEATS AND MILK (FRANK ET AL. 1983; 1985a,b; AND UNPUBLISHED DATA TO 1986)

ANIMAL PRODUCTS	YEAR	% Above 0.1 ug/g	ANIMAL PRODUCTS	YEAR	% Above 0.1 ug/g	ANIMAL PRODUCTS	YEAR	% Above 0.1 ug/g
Beef	1969-70	75.0	Poultry Meat	1969-70	30.0	Cow's Milk	1970-71	36.4
	1971-72	38.4		1971-72	66.0		1973	54.5
	1973-74	51.5		1973-74	25.0		1977	3.9
	1975-76	61.9		1975-76	64.0		1983	1.1
	1977-78	20.0		1979-80	0.0		1985-86	0.0
	1979-80	20.5		1981-82	0.0			
	1981	1.0		1985-86	0.0			
	1985-86	0.0						
Pork	1969-70	66.7	Hen Eggs	1969-70	80.0			
	1971-72	29.2		1971-72	49.2			
	1973-74	37.5		1973-74	87.0			
	1975-76	0.0		1978-80	25.0			
	1979	0.0		1981-82	0.0			
	1981	0.0						
	1985-86	0.0						

legislation was enacted to control the disposal of PCB wastes and to search for alternatives to replace their use in closed systems. Up to 1976, wastes of PCBs were disposed of openly in the environment and resulted in residues reported earlier in agricultural products (Tables E.1 and E.2). Canada enacted similar legislation in 1977.

Some PCB formulations are known to contain PCDF as contaminants.

During the PBB incident in Michigan (Landrigan, 1980), when this compound was inadvertently fed to livestock which resulted in environmental and human exposure, the Ontario border was watched carefully to prevent feed, meat and livestock crossing into Canada. Ontario monitored this situation carefully to minimize the introduction of PBB into Ontario foodstuffs.

Mirex is another persistent toxic industrial product that was used as a fire retardant in household building materials which could potentially accumulate in food. Quantities used in Ontario were small and confined; residues appeared in Lake Ontario fish as a result of manufacturing losses on the U.S. side (Holdrinet *et al.*,1978; Kaiser, 1974). However, no mirex residues appeared in Ontario agricultural produce or animal feed.

E.2.4 Non Agricultural Use of Persistent Pesticides Appearing in Food

The timber and lumber industries use polychlorinated phenol wood preservatives which contain T_3CP, T_4CP and P_5CP together with trace contaminants of the higher chlorinated PCDD and PCDF (See Discussion Section, 1.1.1). Data are presented in Table E.6 showing that detectable residues of T_4CP and P_5CP have appeared in most animal tissues analysed between 1982 and 1986. The highest levels were measured in beef, eggs and milk (Frank, Stonefield and Luyken, 1987). The main source of contamination is believed to be the use of treated wood shavings as animal bedding.

TABLE E.6 : POLYCHLORINATED PHENOLIC RESIDUES IN TISSUES OF DOMESTIC LIVESTOCK AND POULTRY 1982 - 1986. (FRANK, STONEFIELD, LUYKEN,1987)

			NON-DETECTED RESIDUES (No.)	DETECTED RESIDUES (No.)	T_3CP	T_4CP	P_5CP
						(ng/g)	
Forage crops	animal Feed	1982-84	0	14	< 5	10	17
Dairy	milkfat	1982	3	39	<10	<10	
Beef	tallow	1982	0	1	<1	<1	7
	abdominal fat	1985	7	25	<1	<1	6
	abdominal fat	1986	16	4	<1	4	37
	back muscle	1986	4	0	<1	<1	<1
Goat	abdominal fat	1985-86	1	2	<1	<1	5
Rabbit	abdominal fat	1985	4	5	<1	<1	5
Pork	diaphragm muscle	1984	8	17	<1	2	5
	kidney	1984	0	25	<1	4	7
	liver	1984	0	25	<1	4	25
	abdominal fat	1985	4	30	<1	4	25
	abdominal fat	1986	5	15	<1	1	5
	back muscle	1986	3	0	<1	<1	<1
Mutton	abdominal fat	1985	5	9	<1	<1	4
	abdominal fat	1986	7	2	<1	<1	5
Hen	eggs	1986	3	18	<1	4	35
Broiler	abdominal fat	1985	0	11	<1	4	7
	abdominal fat	1985	2	8	<1	2	19
	back muscle	1986	3	0	<1	<1	<1
Turkey	abdominal fat	1985	0	6	<1	<1	5
	abdominal fat	1986	5	0	<1	<1	<1

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